

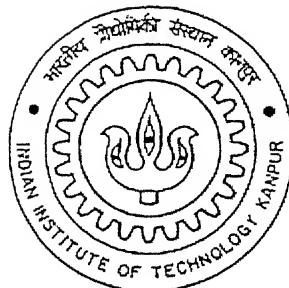
Improved Resistance to Chloride Penetration in Concretes Containing Ground Granulated Blast-Furnace Slag

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

Sharvan Kumar



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

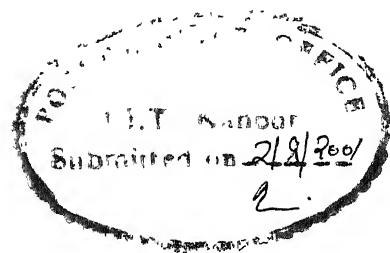
August, 2001

२०१/CE
पुस्तकालय विभाग
भारतीय द्रव्यालय विभाग
द्रव्यालय क्र. 134986



A134986

CERTIFICATE



It is certified that the work contained in the thesis entitled "***Improved Resistance to Chloride Penetration in Concretes Containing Ground Granulated Blast Furnace Slag***" by Sharvan Kumar (9910325) has been carried out under our supervision and that this work has not been submitted elsewhere for the award of a degree.

Dr. Sudhir Misra

Associate Professor,
Department of Civil Engg.,
I.I.T., Kanpur.

Dr. B. Kameshwara Rao

Scientist EII,
Central Building Research Institute,
Roorkee.

July, 2001.

ACKNOWLEDGEMENT

I take this opportunity, with pleasure, to thank my thesis supervisors, Dr. Sudhir Misra and Dr. B Kameshwara Rao for their invaluable guidance, encouragement at every stage of difficulty, critical discussions and continuous support all through the thesis work and especially during final phase of the thesis preparation. I extend my thanks to Dr. Misra and Dr. Rao for their kindness, affection, and support through out my coarse of study and stay at IIT, Kanpur and CBRI, Roorkee.

I would also like to thank Mr. R.K. Goel, Scientist at CBRI, Roorkee, for his help in the chemical analysis part of the thesis. I am also thankful to the staff members, Mr. M.P. Singh, Syambir, Bharat Sigh of concrete testing laboratory at CBRI, Roorkee and Indrapal for their hard work and constant help during the experimental programme.

My special thanks to my friends Alok, Arindam, Jayanta, Onkar, Payal, Rajiv and Shaileendra who made my stay at IIT Kanpur enjoyable and memorable.

Last but not the least, I express my sincere thanks and regards to my parents, brother and sister, without whose support I would never have been in a position to reach at this level and complete this work

Sharvan

TABLE OF CONTENTS

	Page
LIST OF TABLES	x
LIST OF FIGURES	xii
ABSTRACT	xvii
 CHAPTER 1 INTRODUCTION	
1.1 General	1
1.2 Use of ground granulated blast-furnace slag (GGBS)	3
1.2.1 Brief history	3
1.2.2 Present scenario	3
1.2.3 Production of GGBS	4
1.2.4 Advantage of using GGBS	5
1.3 Reinforcement corrosion in concrete	6
1.3.1 Mechanism of corrosion of reinforcing steel and deterioration of concrete	6
1.3.2 Effect of presence of chloride ions	7
1.3.3 Penetration of chloride in concrete	10
1.4 Present work	11
 CHAPTER 2 LITERATURE RIVIEW	
2.1. General	12
2.2. Hydraulic activity of GGBS	12
2.3. Factors influencing slag hydration	14
2.3.1 Glass content of the slag	15

2.3.2 Chemical composition of GGBS	15
2.3.3 Temperature during the initial phase of curing	15
2.3.4 Fineness of GGBS	16
2.3.5 Alkali concentration of the reacting system	16
2.4. Replacement level in cement	16
2.5 Effect of slag addition on properties of fresh concrete	18
2.5.1 Workability and placeability	18
2.5.2 Setting	19
2.5.3 Bleeding	19
2.5.4 Retention of workability (Slump loss)	20
2.5.5 Plastic Shrinkage cracking	20
2.6 Effect of slag on the properties of hardened concrete	21
2.6.1 Influence of curing	21
2.6.2 Heat of hydration	22
2.6.3 Strength	23
2.6.4 Modulus of elasticity	25
2.6.5 Creep and drying shrinkage	25
2.6.6 Autogenous shrinkage	26
2.7. Durability of concretes incorporating GGBS	26
2.7.1 Permeability	27
2.7.2 Resistance to alkali-aggregate reaction (AAR)	28
2.7.3 Resistance against freeze and thaw	28
2.7.4 Resistance to sulfate attack	29
2.7.5 Effect on rate of carbonation	30
2.7.6 Effect on penetration of chloride ions	32

CHAPTER 3 CHLORIDE PENETRATION IN CONCRETE

3.1 Introduction	43
3.2 Mechanism of chloride penetration	43
3.2.1 Diffusion coefficient 'D'	46
3.2.2 Pseudo-equilibrium constant 'Cs'	46
3.3 Measurement and prediction of diffusion coefficient of concrete	47
3.3.1 Conventional techniques	48
3.3.1.1 Conventional and concentrated immersion/ponding test	48
3.3.1.2 Divided diffusion cell	49
3.3.1.3 Rapid chloride migration test	50
3.3.1.4 Modified rapid chloride migration test (Norwegian test)	52
3.3.1.5 Non-steady state migration test	52
3.3.2 Developments using modern techniques	53
3.3.2.1 Impedance spectroscopy	53
3.3.2.2 Nuclear magnetic resonance (NMR)	54
3.4 Concluding remarks	55

CHAPTER 4 EXPERIMENTAL INVESTIGATION

4.1 Introduction	57
4.2 Materials used	57
4.2.1 Cement	58
4.2.2 Ground granulated blast-furnace slag (GGBS)	58
4.2.3 Coarse aggregate	58
4.2.4 Fine aggregate	59

4.2.5 Superplasticizer	59
4.2.6 Water	59
4.3 Proportioning and mixing of concrete	59
4.3.1 Water binder ratio	59
4.3.2 GGBS proportions	60
4.3.3 Water content	60
4.3.4 Coarse aggregate	60
4.3.5. Fine aggregate	60
4.3.6 Superplasticizer	61
4.3.7 Mixing the concrete	61
4.4 Casting and curing of specimen	62
4.5 Experimental procedure	62
4.5.1 Compressive strength test	63
4.5.2 Chloride penetration studies	63
4.5.2.1 simplification in exposure procedure	64
4.5.2.2 Sampling of concrete powder	65
4.5.2.3 Preparation of solution	66
4.5.2.4 Analysis of the prepared solution	67

CHAPTER 5 RESULTS AND DISCUSSION

5.1 Introduction	74
5.2 Results of compressive strength tests	74
5.3 Results of chloride penetration studies	74
5.4 Discussion on compressive strength	75
5.4.1 Results from 100mm and 150mm cubes	75

5.4.2 Strength development in concretes containing GGBS	75
5.4.2.1 Strength at 7 days	76
5.4.2.2. Strength at 28 days	76
5.4.2.3 Long-term strength	77
5.4.2.4 Concluding remarks	79
5.5 Discussion on chloride penetration	79
5.5.1 Discussion on the basis of chloride concentrations at different depths	79
5.5.1.1 Effect of slag replacement level	79
5.5.1.2 Effect of w/b ratio	80
5.5.1.3 Effect of cyclic wetting and drying	80
5.5.1.4 Soluble vs. total chloride	81
5.5.2 Estimated Apparent Diffusion coefficient (D) and pseudo equilibrium surface concentration (C_s)	82
5.5.2.1 Effect of GGBS replacement level	83
5.5.2.2 Effect of w/b ratio	83
5.5.2.3 Effect of exposure concentration	83
5.5.2.4 Effect of cyclic exposure	84
5.5.2.5 Variation of D with age	85
5.6 Chloride diffusion vis-a –vis compressive strength	86
5.7 Diffusion coefficient and service life	87

CHAPTER 6 CONCLUDING REMARKS

6.1 General	127
6.2 Properties of fresh concrete	127
6.3 Strength development in concrete	127

6.4 Resistance to chloride penetration	128
6.5 Quality control in concretes containing slag	129
6.6 Scope for future work	129
 <i>References</i>	
<i>Appendix-1</i>	A-1
<i>Appendix-2</i>	A-5
<i>Appendix-3</i>	A-7

LIST OF TABLES

		Page
4.1	Chemical composition and physical properties of cement	71
4.2	Chemical composition and physical properties of GGBS	71
4.3	Properties of coarse aggregate	72
4.4	Properties of fine aggregate	72
4.5	Characteristics of superplasticizer	73
4.6	Mixture proportions in per cubic meter of concrete	73
5.1	Compressive strength of the concrete mixes at different ages.	90
5.2	Chloride penetration after continuous immersion in 3.5 % NaCl solution.	91
5.3	Chloride penetration after continuous immersion in 7.0% NaCl solution	92
5.4	Chloride penetration after exposure to alternate wetting and drying in NaCl solution, W/B ratio for above is 0.6	93
5.5	Water soluble chloride at 6 week exposure in 3.5% NaCl solution	94
5.6	Water soluble chloride at 24 week exposure in 3.5% NaCl solution	94
5.7	Water soluble chloride at 24 week exposure in 7.0% NaCl solution	95
5.8	Compressive strength at different ages as % of 28 days strength	95
5.9	Diffusion coefficient and surface concentration values obtained by curve fitting from data obtained after continuous immersion in 3.5% NaCl solution.	96
5.10	Diffusion coefficient and surface concentration values obtained by curve fitting from data obtained after continuous immersion in 7.0% NaCl solution.	97
5.11	Chloride penetration results after exposure to alternate wetting and drying in NaCl solution, W/B ratio for all mixes is 0.6	98

age: Diffusion coefficient values (D) in, $10^{-8} \text{ cm}^2/\text{s}$.

LIST OF FIGURES

1.1 Flow-Chart for manufacturing process of GGBS	5
1.2 Schematic representation of the corrosion process	7
1.3 Schematic representation of volume increase due to corrosion	8
2.1 Slump comparison of slag concrete verses Portland cement control [Meusel and Rose, 1983]	38
2.2 Effect of slag fineness on workability of concrete [Meusel and Rose, 1983]	38
2.3 Relationship between heat of hydration and GGBS content (blended cement with 400 and 600 m ² /Kg GGBS fineness) [Tomisawa and Fuji, 1995]	39
2.4 Relationship between fineness of slag and compressive strength [Tomisawa and Fuji, 1995]	39
2.5 Relationship between crystal content of GGBS and strength development of standard ISO mortars (76% slag, 19% clinker, 55 gypsum) [Hootan and Emery, 1983]	40
2.6 Relationship between W/B ratio and compressive strength of slag concrete expressed as percentage of control [Meusel and Rose, 1983]	40
2.7 Progress of carbonation in GGBS concretes (accelerated tests) [Nakamoto and Togawa, 1995]	41
2.8 Relationship between rate of carbonation and water-curing period [Nakamoto and Togawa, 1995]	41
2.9 Reduction in chloride conductivity after immersion in chloride solution at 28 days [Streicher and Alexander, 1995]	42

3 1 Chloride concentration distribution in diffusion cell	50
4 1 Drill-Bit and cube specimen	65
5 1 Strength development in concrete with W/B ratio 0.4	100
5 2 Strength development in concrete with W/B ratio 0.5	100
5.3 Strength development in concrete with W/B ratio 0.6	101
5 4 Compressive strength at 7 days	101
5.5 Compressive strength at 28 days	102
5.6 Compressive strength at 56 days	102
5.7 Compressive strength at 84 days	103
5.8 Compressive strength at 168 days	103
5 9 Percentage increase in compressive strength at 168 days for different replacement levels at different w/b ratios.	104
5.10 Chloride penetration in concrete of W/B ratio 0.4 after 6 week continuous immersion in 3.5% NaCl solution.	104
5 11 Chloride penetration in concrete of W/B ratio 0.5 after 6 week continuous immersion in 3.5% NaCl solution.	105
5.12 Chloride penetration in concrete of W/B ratio 0.6 after 6 week continuous immersion in 3.5% NaCl solution.	105
5.13: Chloride penetration in concrete of W/B ratio 0.6 after 6 weeks exposure to wetting and drying cycles in 3.5% NaCl solution.	106
5.14: Chloride penetration in concrete of W/B ratio 0.4 after 6 week continuous immersion in 7.0% NaCl solution.	106
5.15: Chloride penetration in concrete of W/B ratio 0.5 after 6 weeks continuous immersion in 7.0% NaCl solution.	107

5.16: Chloride penetration in concrete of W/B ratio 0.6 after 6 weeks	107
continuous immersion in 7.0% NaCl solution.	
5.17: Chloride penetration in concrete of W/B ratio 0.6 after 6 weeks	108
exposure to wetting and drying cycles in 7.0% NaCl solution.	
5.18: Chloride penetration in concrete of W/B ratio 0.4 after 12 weeks	108
continuous immersion in 3.5% NaCl solution.	
5.19: Chloride penetration in concrete of W/B ratio 0.5 after 12 weeks	109
continuous immersion in 3.5% NaCl solution.	
5.20: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks	109
continuous immersion in 3.5% NaCl solution.	
5.21: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks	110
exposure to wetting and drying cycles in 3.5% NaCl solution.	
5.22: Chloride penetration in concrete of W/B ratio 0.4 after 12 weeks	110
continuous immersion in 7.0% NaCl solution.	
5.23: Chloride penetration in concrete of W/B ratio 0.5 after 12 weeks	111
continuous immersion in 7.0% NaCl solution	
5.24: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks	111
continuous immersion in 7.0% NaCl solution.	
5.25: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks	112
exposure to wetting and drying cycles in 7.0% NaCl solution.	
5.26: Chloride penetration in concrete of W/B ratio 0.4 after 24 weeks	112
continuous immersion in 3.5% NaCl solution.	
5.27: Chloride penetration in concrete of W/B ratio 0.5 after 24 weeks	113
continuous immersion in 3.5% NaCl solution.	

5.28: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks	113
continuous immersion in 3.5% NaCl solution.	
5.29: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks	114
exposure to wetting and drying cycles in 3.5% NaCl solution.	
5.30: Chloride penetration in concrete of W/B ratio 0.4 after 24 weeks	114
continuous immersion in 7.0% NaCl solution.	
5.31: Chloride penetration in concrete of W/B ratio 0.5 after 24 weeks	115
continuous immersion in 7.0% NaCl solution.	
5.32: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks	115
continuous immersion in 7.0% NaCl solution.	
5.33: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks	116
exposure to wetting and drying cycles in 7.0% NaCl solution.	
5.34 Comparison of chloride penetration in continuous immersion and cyclic exposure at 12 weeks	116
5.35 Comparison of chloride penetration in continuous immersion and cyclic exposure at 12 weeks	117
5.36 Comparison of chloride penetration in continuous immersion and cyclic exposure at 12 weeks	117
5.37: Ratio of soluble after immersion in 3.5% NaCl solution at 6 weeks	118
5.38: Ratio of soluble after exposure to 3.5% NaCl solution at 24 weeks	118
5.39: Ratio of soluble after exposure to 7.0% NaCl solution at 24 weeks	119
5.40: Comparison of soluble chloride at 6 and 24 weeks after exposure to 3.5% NaCl solution	119
5.41: Effect of concentration of immersion solution on apparent diffusion coefficient (D_{app})	120

5.42: Effect of concentration of immersion solution on equilibrium surface concentration (C_s),	120
5.43: Effect of cyclic exposure on apparent diffusion coefficient at 6 weeks	121
5.44: Effect of cyclic exposure on apparent diffusion coefficient at 6 weeks	121
5.45: Effect of cyclic exposure on apparent diffusion coefficient at 6 weeks	122
5.46: Apparent diffusion coefficient of concrete with w/b ratio 0.4, exposed to continuous immersion in 3.5 % NaCl solution.	122
5.47: Apparent diffusion coefficient of concrete with w/b ratio 0.5, exposed to continuous immersion in 3.5 % NaCl solution.	123
5.48: Apparent diffusion coefficient of concrete with w/b ratio 0.6, exposed to continuous immersion in 3.5 % NaCl solution.	123
5.49: Apparent diffusion coefficient of concrete with w/b ratio 0.6, exposed to alternate wetting and drying cycles in 3.5 % NaCl solution.	124
5.50: Apparent diffusion coefficient of concrete with w/b ratio 0.4, exposed to continuous immersion in 7.0 % NaCl solution.	124
5.51: Apparent diffusion coefficient of concrete with w/b ratio 0.5, exposed to continuous immersion in 7.0 % NaCl solution.	125
5.52: Apparent diffusion coefficient of concrete with w/b ratio 0.6, exposed to continuous immersion in 7.0 % NaCl solution.	125
5.53: Apparent diffusion coefficient of concrete with w/b ratio 0.6, exposed to alternate wetting and drying cycles in 7.0 % NaCl solution.	126

ABSTRACT

Use of slag (ground granulated blast-furnace slag, GGBS) is beneficial in reinforced and mass concrete for reducing hydration temperature and improving pore structure. Its use is especially beneficial from durability point of view when concrete is exposed to severe exposure condition such as seawater etc. Structures exposed to such environment are attacked by chloride and sulfate ions and it has been found that due to chloride attack, the reinforcing bars become vulnerable to corrosion.

This work is focused on improvement in resistance to chloride penetration due to incorporation of slag in concrete. The compressive strength development in concretes containing slag has also been studied upto a bath-cured age of 168 days, for different slag replacement levels. The studies have been conducted on twelve mixes of similar workability with three water binder ratios of 0.3, 0.4 and 0.5 and three replacements of OPC by GGBS of 35, 55 and 75% along with control OPC concrete with no GGBS. Chloride penetration studies have been carried out using conventional immersion test for exposure ages of 6, 12 and 24 weeks. The specimens were exposed to 3.5 and 7.0% sodium chloride solutions in continuous immersion as well as cyclic wetting and drying.

The results of study show that though there is slow initial strength development in GGBS concretes, they continue to gain strength till longer period and ultimate strength obtained is comparable or higher compared to control OPC concretes. There is also great improvement in resistance to chloride penetration due to incorporation of GGBS, which increases with increase in replacement level. Improvement in resistance to chloride penetration (pore refinement) is obtained, even if compressive strength is adversely affected (at larger levels of replacement). Though at lower ages the results are inconclusive the difference in resistance to chloride penetration is considerably high at higher exposure durations.

Key words: reinforced concrete; ground granulated blast furnace slag (GGBS); blended cement; compressive strength; bath curing; corrosion; diffusion; diffusion coefficient; pseudo equilibrium surface concentration.

Chapter 1

INTRODUCTION

1.1 General

Reinforced concrete is the most widely used building material at present and is being used to construct almost all kinds of civil engineering structures – buildings, bridges, dams, roads, etc. Its wide popularity and acceptance is due to its excellent resistance to degrading agents, the ease with which ‘green’ concrete can be moulded into different shapes and sizes to build a variety of structural elements, and easy availability of raw materials. Seeing the enormous use of concrete in construction industry, it is also a very attractive proposition for safe disposal and economic utilization of huge quantities of waste and by-products containing cementitious properties. In this context, pozzolanas and slags have proved to be very promising ingredients of concrete. Their use has become inevitable due to their advantageous properties leading to increase in durability of structures, conservation of energy and ecosystem and, economic construction and maintenance. Still, the rate of utilization of these cementitious by-products is dismally low in many countries, including India. To promote their use in concrete construction, it is necessary to build confidence among the users and demonstrate that use of these materials does not compromise the good properties of concrete and may even enhance the durability of concrete, if used judiciously.

There are numerous surviving ancient buildings and monuments standing like legends, while so much of damaged infrastructure built by using Portland cement requires frequent repairs and rebuilding. The cementitious materials used in these ancient structures give us some clue about the use of pozzolanic materials in concrete for enhancing its durability. Some examples of pozzolanic durability are about 2000 years

old harbour installations along the Mediterranean sea, built by Greeks and Romans, the Pantheon (125 A.D.) in Rome, the Suez canal (1860) in Egypt, and the Corinth canal (1881) in Greece. The mortars used in the harbour installations built by the Greeks and the Romans had six parts volcanic ash, two parts lime, and one part of fine sand.

There is great awareness now about the durability of buildings and other structures because of the growing cases of premature failures and the rapidly increasing costs of repairs and maintenance. So, there is a need to include the 'life-cycle' cost of structures rather than their construction cost alone in determining the economics of construction.

A review of past literature clearly identifies fly-ash (obtained from thermal power plants), blast-furnace slag (obtained from iron & steel industries) and micro-silica (obtained from silicon processing plants) as possible 'additives' in cement concrete. Research has shown that these materials, when blended with cement, are capable of increasing the durability of concrete structures significantly. Of these materials, GGBS (Ground Granulated Blast Furnace Slag, processed from blast furnace slag) has been taken for study in this work.

The other aspect encouraging the use of slag in concrete is the conservation of energy and ecosystem. As we know that cement industry is one of the most energy intensive industries, so a replacement of cement by byproducts of another industry leads to a great saving of the exhaustible resources of energy and saves the environment from pollution. The use of by-products on one hand solves the problem of waste management and on other hand saves the valuable resources.

1.2 Use of ground granulated blast-furnace slag (GGBS)

1.2.1 *Brief history*

The use of blast furnace slag in the construction industry was initiated by Loriot as early as 1774, when he made a mortar using slag in combination with slaked lime [Mather, 1957]. Langan produced the first cement from water-granulated slag in Europe in 1863. Slag-lime cements were commercially developed and used in 1865 in Germany. In France, these slag cements were used as early as 1889 to build the Paris under ground metro system. Since the late 50's use of GGBS as a separate cementitious material added to the concrete has gained wide acceptance in United states, United kingdom, France, and other parts of Europe, South Africa, Australia, Netherlands, Japan, and many other countries of the world. In India, though Portland slag cement (PSC) is in use for over 35 years, use of GGBS (mixed at the concrete mixer) in any big project started only 5 years ago, i.e. in 1996. It was used by AFCONS Infrastructure Ltd., Mumbai on the advice of its German consultant Dwydag for laying a 3.5 km long sewage disposal pipeline under sea near Mumbai. In this project 70% GGBS and 30% OPC was used [Rajkumar, 1998].

1.2.2 *Present scenario*

Presently granulated blast furnace slag (GBS) is used in two ways: (a) by intergrinding with portland cement clinker along with gypsum and using this blended cement at the time of manufacture and, (b) as a separately ground cementitious material (ground granulated blast-furnace slag) blended with cement while mixing concrete mixes. In general, the slag content of cement varies from 10 to 95 percent depending on the requirements needed for the job. The Indian Standard on Portland slag cement, PSC, (IS: 455-1989) permits addition of 25 to 65 percent of GBS. However, the dosage of slag adopted by the plants in the manufacture of PSC usually ranges up to 50 percent. Use of

GGBS along with OPC (Ordinary Portland Cement) in concrete is allowed under BS 6699:1992 and ASTM C 989:1995. But there is no Indian Standard yet for GGBS.

Europe has a long tradition of using GGBS as a special cementitious material blended with OPC in proportion up to 80% and has a very good performance track record. In India, also the use of blast furnace slag in the production of PSC (Portland Slag Cement) began long back, but the recent attention has been given to the use of GGBS as a separate cementitious material. According to a report cited by Sharma and Mohan, 1999, in India, about 10.95 million tones of blast furnace slag was generated in the year 1996-1997 from the integrated steel plants alone, but out of that only 3.8 million tones was in granulated form.

1.2.3 Production of GGBS

Blast-furnace slag is a by-product of iron and steel industry. It is obtained during 'smelting' of iron ore in blast furnace. The slag in blast furnace, which is in molten state, floats on the top of molten iron and below the unmelted burden. To maximize the hydraulic properties the molten slag is chilled rapidly (the process is known as 'quenching') immediately after it leaves the blast furnace. The most commonly used method of quenching slag is water-granulation. Modern granulation systems use high - pressure water jets that impinge on the stream of molten slag at a water-slag ratio of about 10 to 1 by mass. The blast furnace slag is quenched almost instantaneously to a temperature below the boiling point of water, producing highly glassy particles. Granulated slag is then dewatered, dried, and, ground fine to give Ground Granulated Blast Furnace Slag (GGBS). A self-illustrative diagrammatic view of the production of Ground Granulated Blast-Furnace slag is given in Figure (1.1).

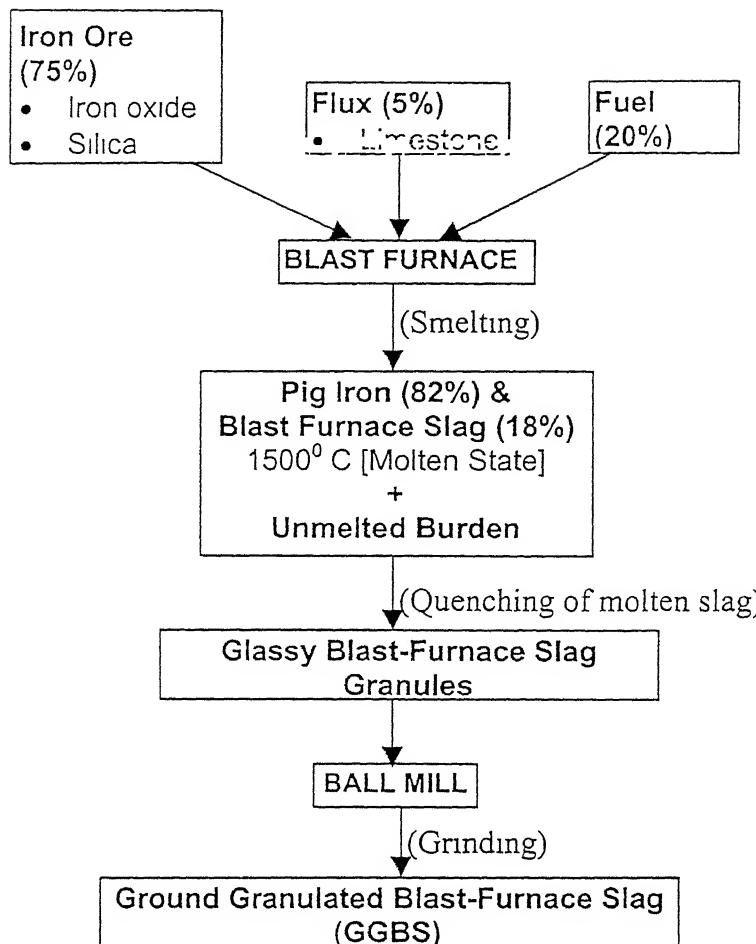


Figure 1 1: Flow-Chart for manufacturing process of GGBS

Due to the highly controlled addition of the raw material to the furnace, there is very low variability in the composition of iron and slag obtained from a particular plant. The blast-furnace slag thus obtained contains cementitious properties, and is able to provide stiffness and durability to concrete structures.

1.2.4 Advantage of using GGBS

Mixing slag in concrete has been reported to have the following advantages:

- Reduction in heat of hydration;
- Increased chemical resistance;
- Pore refinement and reduced permeability.

The ways and the extent of manifestation of above improvements directly affecting the

durability of concrete are dealt in detail in the chapter 2 of this work. Permeability to aggressive water controls the physical and chemical process of degradation. Chloride penetration in concrete is of tremendous importance with regard to durability of reinforced concrete structures, as it is known to promote corrosion of reinforcing bars.

1.3 Reinforcement corrosion in concrete

It may be noted that the present work is largely focused on pore refinement and increased resistance to chloride penetration in concretes containing slag. Thus, though it is out of the preview of the present work, a brief explanation of the mechanism of reinforcement corrosion, and effect of presence of chloride ions on it, is discussed in this section. This has been done to put in perspective the importance of a more refined pore structure from the point of durability of concrete structures.

1.3.1 Mechanism of corrosion of reinforcing steel and deterioration of concrete

Corrosion of steel embedded in concrete is a oxidation-reduction reaction resulting in oxidation of iron present in steel. The reactions proceed by means of an electrochemical mechanism, which involves both microcell and macrocell corrosion [Gulikers et al, 1996]. The electrochemical potentials needed to form these corrosion cells may be generated in RCC in two ways:

- i) Composition cells are formed due to non-uniformity in the surface characteristics of the reinforcing steel.
- ii) Concentration cells are formed due to differences in concentration of dissolved ions in the vicinity of steel.

As a result of creation of these potential differences some part of the embedded steel becomes anodic where as some other part becomes cathodic and an electrochemical

current comes into existence. The above phenomenon is diagrammatically illustrated below in Figure (1.2).

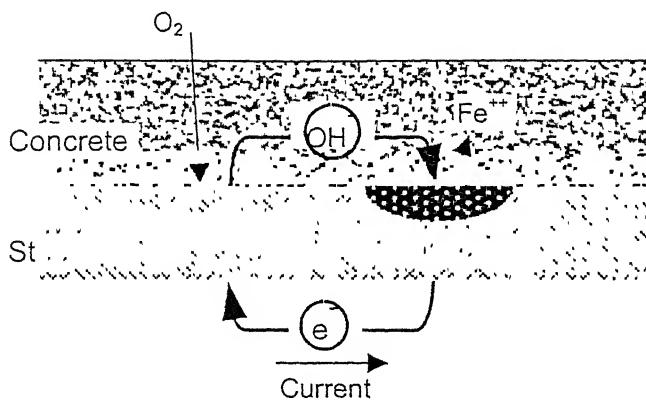
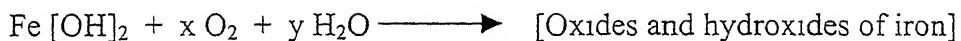
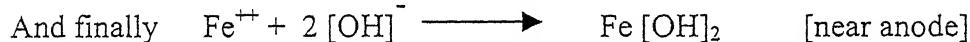
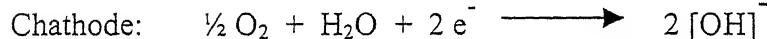


Figure 1.2 Schematic representation of the corrosion process

The chemical reactions occurring in the process of corrosion are:



The transformation of iron to rust is accompanied by an increase in volume, which, depending on the state of oxidation may be as large as 6 times to that of the original metal. The relative volume of different corrosion products with respect to the original volume of iron is diagrammatically presented below in Figure (1.3).

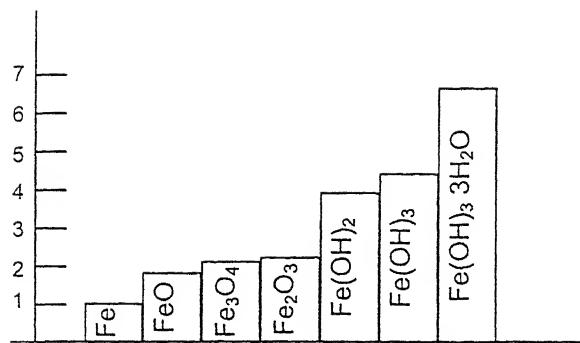


Figure 1.3: Schematic representation of volume increase due to corrosion

This increase in the volume of reinforcing bars causes cracking of concrete cover and finally their spalling. The local pitting of iron also leads to reduced cross-sectional area of reinforcing steel at particular sections, and could result in structural distress.

1.3.2 Effect of presence of chloride ions

Presence of chloride ions is detrimental for the reinforcement in concrete. It is due to the fact that chloride ions, if present in the pore solution of concrete, have adverse effect on the protecting film present over the reinforcing bars. The reinforcing steel is generally protected from corrosion if good quality concrete is used and sufficient concrete cover is provided over the reinforcement. The resistance of the embedded steel against corrosion can be attributed to:

- Highly alkaline environment inside concrete.
- Its low permeability

In general a thin layer of iron oxide covers iron products. In a highly alkaline environment, which is provided by concrete (the alkaline environment is due to presence of large amount of Ca(OH)₂ produced as a result of hydration of cement), this thin ferrous oxide layer becomes impermeable and very stable, thus denying direct access to the metallic iron, disrupting the anodic process. Further corrosion cannot take place until

this protective layer is somehow destroyed. The protective layer of passive iron oxide can become active and unstable due to two reasons:

- Lowering of pH of the pore solution
- Ingress of Cl^- ions into the concrete

The pH of the concrete pore solution is about 13.0 when suitable amount of OPC is used and is slightly lower, that is about 12.0-12.5 when, admixtures like slag or fly ash are used. In the absence of Cl^- ions, the protective film on steel is reported to be stable as long as the pH of the pore solution near the steel is above 11.5. But it has been observed that the presence of Cl^- ions can cause the depassivation of reinforcing steel even at pH values considerably above 11.5, thus initiating corrosion.

It has been reported [Mehta] that, when Cl^-/OH^- ratio rises above 0.6, steel seems to be no longer protected against corrosion. Similarly, although there is not a total agreement about the Cl^- content threshold below which the passivity of steel reinforcement is maintained, usually the limit is taken as 0.4% and 0.2% by weight of cement for RCC and prestressed concrete respectively [Climent et al, 1999]. This means that the Cl^- ion content in the vicinity of reinforcement should be below 0.08% by weight of concrete. The threshold value of 0.4% mentioned above, which is adopted by many codes of practice also, is a conservative one. Polder et al, 1996 suggests that for low water/binder ratio concrete, subjected to frequent wetting and drying (considered as most severe exposure condition), the initiation of corrosion may require a Cl^- concentration as high as 1% by weight of binder i.e., 0.17%-0.20% by weight of concrete, if the concrete is not carbonated.

Besides destroying the passivating layer, the damaging effect of presence of Cl^- ions is manifested in one more ways. The presence of large amount of Cl^- ions increase the water holding capacity of concrete in turn lowering its electrical resistivity and hence

increasing the corrosion current. After the destruction of the protecting film, electrical resistivity of concrete and availability of O_2 near cathodic sites are the sole factors, which control the rate of corrosion. In addition to these effects on the corrosion of reinforcing steel, crystallization of salts in pores of concrete may also result in disruption owing to pressure exerted by crystal growth.

1.3.3 Penetration of chloride in concrete

From the above discussion it is clear that ability of concrete to resist the penetration of chloride ions is a critical parameter in determining the service-life of steel-reinforced concrete structures exposed to deicing salts or marine environment (contains about 3.5% salt, predominantly chlorides). Therefore, it is impermeability of concrete, which is the most desirable property of concrete for protection of reinforcement against corrosion. The low permeability is usually obtained by the use of low water/binder ratio, proper grading of aggregates and, now a days, by using mineral admixtures in concrete such as fly ash and slag. The addition of mineral admixtures to concrete reduces the pore size in concrete and also increases the tortuosity of the pore system.

In addition to the above controls proper concrete cover is provided over the reinforcement so that the time required by the penetrating Cl^- ions to reach the threshold value is increased. But while doing so, it has to be kept in mind that the flexural crack widths, which increases with increase in concrete cover and diameter of reinforcement, also remain in limit. So, there is a limit to which cover can be increased and therefore impermeability is of paramount importance. In submerged and saturated concretes, chloride penetrates mainly via diffusion of Cl^- ions and hence the diffusion coefficient of concrete gives indirect measure of permeability of concrete to chloride penetration. Another quantity that affects the diffusion of chloride ions is the equilibrium surface chloride concentration of the concrete. It has been found that the concentrations of

chloride reach saturation comparatively quickly at the surface of concrete, and this concentration is much lower than the concentration of the exposure solution. Higher the value of the equilibrium surface concentration higher will be penetration of chlorides.

It should also be noted that chloride is present in concrete in bound as well as free state, and it is the free chloride present in pore solution that causes the depassivation of protecting film over the steel. So, use of ingredients that can bind Cl^- ions, such as cement with higher C_3A content, might be thought beneficial. But, higher C_3A content is not desirable in view of resistance against sulfate attack, and in majority of the cases chlorides and sulfates are encountered together by the concrete.

1.4 The present work

A survey of literature clearly establishes the fact that blended cement, especially those containing GGBS, have a better chloride penetration resistance. It may also be noted that the properties of concrete containing GGBS are very closely related to the chemical composition, glass content, and fineness etc. of the GGBS. Therefore, need was felt to obtain quantitative information in this regard using currently available slag and cement.

Present study has focused on:

- i. Experimental investigation of the penetration of chloride ions in concrete and the effect of different percentages of slag used as binding material
- ii. Experimental investigation of strength development in concretes having different percentages of slag and their comparison with the concretes containing only OPC.
- iii. Estimation of the apparent diffusion coefficients and pseudo equilibrium concentrations from the chloride concentration profiles obtained at different ages of exposure.

Chapter 2

LITERATURE REVIEW

2.1 General

Since the late 50's use of GGBS as separate cementitious material added to the concrete has gained acceptance in many countries of the world. Its various uses all over the world have shown a very good record of accomplishment, especially highly increased resistance to aggressive environment. The most commonly known property of concrete i.e. the compressive strength is also found to be comparable to that of OPC (Ordinary Portland Cement) concrete at the age of 28 days, and even greater at later ages. However, the initial development of strength has been reported to be slow in GGBS concrete. The permeability or diffusion of chloride ions in the concrete is greatly reduced due to the use of GGBS, in some cases the reduction in the diffusion coefficient has been reported to be as high as 25 times.

Extensive work has been carried out in the last 50 years to better understand the effect of adding GGBS on properties of concrete. An effort has been made to present a brief summary in this chapter of the work, especially relevant from point of view of chloride penetration in concretes containing GGBS.

2.2 Hydraulic activity of GGBS

It is very much accepted that the principal hydration products formed by GGBS are the same as that formed by the OPC, i.e. calcium silicate hydrate (CSH). Only thing is that the ratio of calcium to silica in the CSH produced by the GGBS is found to be lower and this is why GGBS is capable of binding more alkali than OPC [Regourd 1980]. When water is added to pure GGBS, the initial hydration is much slower than the

OPC. To accelerate the hydration process some activator is required. Activators promoting the hydration of GGBS are generally of two kinds – alkaline activators such as sodium hydroxide, lime etc. or sulphate activators such as calcium sulphates, phosphogypsum etc. [Mesto and Kajaus, 1983; & Roy, 1989]. From practical point of view, Portland cement (OPC) is the best activator, as it is already there as an important ingredient of concrete. Hydration of GGBS in presence of OPC takes place predominantly due to breaking of the glassy structure by the hydroxyl ions released during to the hydration of cement. The glass in blast furnace slag consists of monosilicates like those in Portland clinker. When activated the blast furnace slag dissolves. This activation of slag begins at relatively low pH's, in general between 11 and 12 [Bijen, 2000].

According to studies conducted by D.M.Roy [1989] the alkaline activators accelerate the dissolution of Si and Al ions by breaking the Si-O and Al-O bonds in the slag glass structure, which is followed by precipitation of low solubility calcium silicate and aluminate hydrates due to increased ionic concentrations in the liquid phase. When gypsum is present then the dissolved Si and Al ions react with gypsum in high pH environment to form ettringite ($C_3A \cdot 3CS \cdot H_{32}$). It is also observed that when pH of the liquid phase reaches approximately 12, the hydration is most accelerated. The author further states that the addition of slag gives rise to different characteristic of hardened materials arising from both chemical reactions and physiochemical effects. From analysis of 4-year-old pastes Roy found not only lower C/S ratios in blended cement pastes, but also higher alkali retention. The physiochemical effects affect the rheological properties of fresh concrete and the microstructure of the hardened paste, which are generally favourable. Of particular interest is the reduction in the mean pore radius, which is reported to be near 2 nm in blended paste compared to nearly 9 nm in OPC

pastes. This pore refinement has great effect on permeability and other related properties of mortars and concretes incorporating GGBS.

Regourd [1980] and Idron [1983] suggest that the hydration of GGBS takes place in two stages. Initially the predominant reaction is with alkali hydroxide, but later reactions with calcium hydroxides predominate. Since this calcium hydroxide comes from the hydration of cement only, the major amount of GGBS hydration lags behind that of OPC. Tanaka et al, 1983, also investigated and published the hydration mechanism of a glassy slag, its morphological aspects, and the structure of the slag hydrates. In general the pore water of the hardened slag cement concrete is somewhat less alkaline than that of Portland cement concrete. This is not because the total amount of alkaline constituents is less, but because more alkali metals, i.e. sodium and potassium, are bound in the cement paste [Fraaji et al, 1989].

2.3 Factors influencing slag hydration

Understanding the phenomenon of hydration of GGBS, we can well conceive the factors, which affects its cementitious properties. The cementitious quality of slag can be most easily established by determining the strength development of the concrete specimen cast using it. Especially the contribution of the slag to the initial strength development is a good indication of the latent hydraulic activity of the slag. The dominant factors affecting the hydraulic properties of slag are glass content of GGBS, its chemical composition, curing temperature, fineness, alkali concentration of the reacting system etc. However, the acceptance criteria for suitability of slag should not be based on these physical and chemical characteristics of slag, and the actual performance of the concrete specimens i.e., compressive strength development is still more realistic and reliable.

2.3.1 Glass content of the slag:

It is the most important factor affecting the hydration of granulated blast furnace slag. The active part of the slag is its amorphous glass content. A good quality slag should consist of more than 85% of glass. The British Standard BS. 6699 - 1992 specifies a minimum glass content of 67%. But researchers have not found any correlation of glass content to hydraulic activity as yet. This is because of the number and complexity of the influencing factors and the uncertainty involved in determining the glass content accurately. Hooton and Emery [1983] tried to find some correlation between the hydraulic indices and the physical and chemical properties especially chemical composition and glass content of the slag, and they found the best correlation at the age of 7 days. However, the scatter in the index equation was still much high. While it is generally believed that the strength of concrete increases with increasing glass content of the slag used, some researchers like Demoulian et al [1980] have found that with glass content in excess of 95% the strength is reduced, Figure 2.5.

2.3.2 Chemical composition of GGBS:

It is also an important factor affecting the hydraulic properties of GGBS. It determines the basicity of the slag and the structure of the glass. In general, the hydraulic activity increases with increasing content of lime and alumina, and with decreasing content of silica and magnesia. The chemical composition of GGBS depends upon the composition and quality of iron ore and fluxes used for the smelting of pig iron.

2.3.3 Temperature during the initial phase of curing:

Ambient temperature during the initial phase is another important factor that determines the rate of strength development. Concrete incorporating GGBS is found to respond very well under elevated temperature curing. With increasing temperature the solubility of alkali hydroxides and calcium hydroxide also increases, which promotes the

early reactions of GGBS. As reported by Hogen and Mousel [1981] for accelerated curing conditions we can get 1 day compressive strength of concrete incorporating GGBS higher than that containing only OPC. On the other hand at normal or lower temperatures we get lower strength for GGBS concrete at early stages

2.3.4 Fineness of GGBS:

The fineness of slag, which is measured in terms of specific area using Blaine's air permeability test, is again a very important factor governing the rate of hydration of GGBS. Higher fineness leads to early strength development. A concrete having very-fine GGBS can have satisfactory strength development even at curing temperatures as low as 5°C. Whereas, concrete containing coarser GGBS may require heat curing for improving strength development at early ages [Miura et al, 1998]. Since the reactions of GGBS are rather slower than that of OPC, the GGBS is generally ground finer than the OPC. However, in practice fineness of GGBS is limited by the economic factors and performance considerations such as setting time and shrinkage [Swamy, 1999]. And it is this economic advantage, which has lead to the practice of grinding the Granulated Slag separately in most countries.

2.3.5 Alkali concentration of the reacting system:

It has already been pointed out that reactions of slag begin after its glassy structure is broken down and the particles are dissolved into the alkaline activator, which is calcium hydroxide produced during the hydration of cement in this case. More the concentration of alkali present in the concrete matrix faster will be the reaction of slag with these alkali compounds.

2.4 Replacement level in cement

Researchers have reported changes in the properties of fresh and hardened concrete at different levels of replacement (of OPC) by the GGBS. The replacement

levels range from 20-90%, and apparently depend upon the purpose for which concrete is to be used, the curing temperature, and the quality of GGBS and OPC used.

From strength point of view, there seems to be an optimum blend of GGBS and OPC that produces the greatest compressive strength. The optimum blend giving highest strength is usually found to be 50% GGBS and 50% OPC [Tomisawa & Fuji, 1995]. But there are other factors also, such as control of temperature rise in mass concrete structures, time of setting, sulphate resistance, resistance to expansion due to alkali aggregate reactions, corrosion of reinforcing steel etc. which are often considered when discussing the 'optimum' level of cement replacement. And they are these factors concerning the durability of concrete, which have raised the concern and have led to the use of materials like GGBS in concrete. These factors demand higher replacement of OPC by the GGBS. Strength gain can be improved by improving fineness of GGBS and using higher percentages of slag can reduce heat of hydration. With use of Blaine's fineness greater than $600 \text{ m}^2/\text{kg}$ and over 80% slag content we can get a concrete with lower heat of hydration and good compressive strength even at early ages [Tomisawa et al., 1995]

Having discussed the important factors affecting hydraulicity of GGBS and knowing the effect of GGBS on the properties of concrete one can decide the replacement level of slag to be used for any specific purpose. For example some of the criteria for ascertaining the slag percentage are as given below:

- a. The percentage of slag depends on the glass content and reactivity of slag; higher the glass content and the reactivity, higher can be the percentage of GGBS;
- b. Higher slag contents delay the setting and give lower levels of strengths at early ages;
- c. When the reduction of heat of hydration in concrete is the criterion, it is better that

GGBS content of the cement + slag binder is 50 percent or more;

- d. When a GGBS is intended to be used in concretes to resist sulphate attack, chloride penetration, effects of sea water, acid attack etc., then the slag content should be kept at least 60 to 65 percent;
- e. When slag concrete is expected to resist carbonation, the thin structural members, and where columns and beams are made out of slag concrete, the slag content should not exceed 50 percent of total cementitious material [Osborne, 1989]. This precaution is only for interior members of buildings and for both interior and exterior members in draughty areas;

While making the concrete mix it should be noted that the specific gravity of slag ranges from 2.85 to 2.95, compared to 3.15 for Portland cement. Thus, a given replacement of cement by slag on a weight basis results in higher volume of paste in a concrete mixture, which may affect the rheology of concrete mixture, at higher replacement levels.

2.5 Effect of slag addition on properties of fresh concretes:

2.5.1 *Workability and placeability:*

It has been reported that concretes containing blast furnace slag usually exhibits superior workability, compared to OPC concretes of the same properties [Meusel & Rose, 1983, Robins et al, 1987]. The workability of slag concretes was found to increase, with the percentage of slag, for the same water/cementitious ratio. It was reported that, if the fineness of slag is more than the cement, then the blended cement gives better workability. If the slag has lower fineness than that of cement, then the PSC gives slightly lower workability [Robins et al, 1987]. According to Meusel and Rose, there is slight decrease in workability with increasing fineness of GGBS but the effect is

not very significant. In general, the higher cohesive property is very much helpful in placing the concrete. Fluton suggested that cementitious matrix containing GGBS exhibit greater workability due to the increased paste content and increased cohesiveness of the paste [ACI committee 233-2000]. Fluton also reported that concrete containing blast furnace slag need less vibration for a certain degree of compaction than the plain cement concretes. But, this phenomenon is not well documented and needs specified field experiments for confirmation.

2.5.2 *Setting:*

Usually an increase in the time of setting can be expected, when GGBS is used in concrete. The degree, to which the time of setting is affected, depends on slag content in cement and ambient temperature at the time of curing. This may lead to delay in the removal of formwork.

At temperatures below 23°C, considerable retardation in setting can be expected for slag concretes compared to OPC concretes, which has serious implications in winter concreting. Although significant retardation has been observed at low temperatures, the additions of accelerators can greatly reduce this effect. At higher temperatures ($>30^{\circ}\text{C}$), there is little change in setting time of GGBS concretes as compared to OPC concretes [Hogan & Meusel, 1981].

2.5.3 *Bleeding:*

Bleeding in fresh concrete depends on the total surface area of the solids and the amount of water used in concrete. The total surface area depends mostly on the fineness of cementitious material used. Therefore when GGBS is used in concrete, its effect can be visualised depending upon the fineness of the GGBS as compared to the OPC. Also temperature at the time of casting may have an influential effect on bleeding, as low ambient temperatures at the time of placing delay setting of concrete. There are chances,

that delayed setting may cause bleeding. Accordingly ground slag, blended with OPC may increase bleeding at low ambient temperatures

2.5.4 *Retention of workability (Slump loss):*

It is a general observation, as reported by some of the researchers and also experienced in practical work, that the slag concretes exhibit lower slump loss than OPC concretes. But Meusel and Rose [1983] indicate that concrete containing 50% GGBS shown slum loss equal to that of concrete without containing GGBS. Normally, GGBS exhibit slower rate of reactions and lower rate of heat of hydration, which manifest in delay in stiffening of concrete. The delay in stiffening lowers slump loss. The lower slump loss facilitates transporting of green concrete to longer distances, and thus it is more useful in ready mixed concreting.

2.5.5 *Plastic shrinkage cracking*

GGBS and Fly ash are specially recommended in hot climates for production of durable concretes, due to their ability of decreasing temperature rise due to heat of hydration. But several investigators have raised concern about the need for continued and enhanced curing, when materials like slag are used, especially in hot and arid environments. Though relative humidity is the main factor influencing plastic shrinkage and if curing is done properly it can be avoided, it has been reported that the rate of water evaporation in the blended cement concrete is higher than that in the OPC concrete exposed to similar temperature and humidity. Further, bleeding in the blended cement concretes is less than that in plain cement concrete. The cumulative effect of these two parameters results in increased plastic shrinkage cracking of blended cement concretes [Almussalam et al, 1999]. Even though they noted development of cracks earlier in plain concretes, the total area of cracks in the blended cement concrete specimens was more than that in plain cement concrete.

In comparison to the other blended cements, the blast furnace slag cement concrete specimens shown higher plastic shrinkage cracks in the study of Almussalam et al. the higher area of cracks in GGBS concrete may be attributed to higher replacement levels, slow strength gain and low tensile strain capacity at early ages.

2.6 Effect of slag on the properties of hardened concretes:

2.6.1 *Influence of curing:*

Concretes containing GGBS are found to be more susceptible to poor and inadequate curing [Swamy & Boukini, 1990]. GGBS concretes are especially very sensitive to the curing temperatures and the duration of moist curing when the percentage of GGBS in the total cementitious material is more than 30%. It can be described on the basis that the rate and degree of hydration of cement paste and consequently its strength gain is affected significantly by the rate of loss of moisture, which is required for hydration, at an early age. In the case of GGBS concrete the rate of hydration is slow in the initial period leading to increased loss of moisture, if curing is not done properly, leading to a decrease in strength gain [Fluton, 1974]. This effect becomes more pronounced, when the concrete contains higher percentages of slag. Thus, to ensure proper strength development and durability of the concretes incorporating GGBS, it is important that these concretes are paid more attention, regarding moist curing. The effect of curing methods, humidity and ambient temperature on the strength of concrete incorporating GGBS has been well studied and documented by Chern and Chan in 1989, and that especially in cold regions by Miura and Iwaki in 1998.

Japan Society of Civil Engineers (JSCE) subcommittee recommends different duration for moist curing for concrete containing different percentages of slag at different ambient temperatures. These details are reproduced in table given below:

Minimum time required in days for moist curing of slag concretes

Ambient temperature during curing	Percentage of slag		
	30-40	40-55	55-70
17°C or above	5	6	7
10°C-17°C	7	8	9
5°C-10°C	9	10	11

2.6.2 Heat of hydration:

The most important contribution of slag to concrete that is widely known more than any thing else, and which in fact initiated its use in concrete construction, is its ability to reduce the rate of evolution heat of hydration, which is evolved due to the exothermic reactions of cement and water. At higher replacement levels, GGBS is capable of significantly reducing the maximum temperature rise due to heat of hydration. It not only causes the reduction in peak temperature produced, but also delays its occurrence [Swamy, 1999]. In addition to that it has been found that the thermal coefficient of expansion of GGBS concrete is also less than that of OPC concrete. Thus the use of GGBS reduces not only the thermal gradient in side the concrete but also the strain differentials associated with them. As given by Swamy the temperature strain relationship for different percentages of GGBS replacement is as follows:

$$\text{OPC + 0% Slag} \quad 9.0 \times 10^{-6} \text{ per } {}^{\circ}\text{C}$$

$$\text{OPC + 30% Slag} \quad 8.0 \times 10^{-6} \text{ per } {}^{\circ}\text{C}$$

$$\text{OPC + 70% Slag} \quad 7.5 \times 10^{-6} \text{ per } {}^{\circ}\text{C}$$

This potential of supplementary cementitious materials like GGBS and Silica Fume has been advantageously harnessed for the production of high-performance concrete (HPC), yielding 28 days compressive strengths as high as 100 Mpa [Lim &

Wee, and, Sanjayan & Sioulas, 2000]. Some estimates of heat reduction are shown in the following table, based on tests carried out by Portland Cement Institution (PCI), South Africa (Addis).

Reduction of heat of hydration of Portland slag cement (PSC) concretes

<i>Slag</i>	<i>% Reduction of heat of hydration compared to OPC concretes</i>	
	<i>After 3 days</i>	<i>After 7 days</i>
30	10-15%	0-10%
50	20-25%	5-15%
70	35-45%	30-35%

From the above table, it can be noted that the heat-reducing benefits of slag cements are more pronounced during first three days, and that significant drop in heat generation occurs, when slag content rises above 50 percent.

2.6.3 *Strength:*

Compressive strength is the most fundamental of concrete parameters in structural design, and is also often used as a basis to determine many other engineering properties of concrete. Hence it is a major criterion for judging the suitability of GGBS as a cementitious building material. The compressive as well as flexural strength development of GGBS concrete has been found to be slower at early ages than the corresponding OPC concrete, regardless of the replacement percentages and the fineness of GGBS at normal ambient temperatures. But, if higher fineness of GGBS is used and the curing temperature is maintained high then we can get an accelerated strength development. At the age of 28 days, the compressive strength of concrete incorporating higher-grade GGBS approaches to that of the OPC concretes, and beyond this period while the strength gain in OPC concretes is insignificant, the GGBS concrete continue to gain strength. Thus at later ages i.e. on 56 days or 91 days we get higher strength in

GGBS concretes than that of OPC concrete having same water-binder ratio. The above-mentioned property of GGBS concrete has been observed by numerous investigators, some of whom are Hogan and Meusel [1981], Nakamoto and Togawa [1995], Swamy [1999] and, Lim and Wee [2000].

As reported by many researchers the compressive and flexural strength characteristics of concrete containing GGBS depends upon a large number of factors, such as water to cementitious material ratio, curing temperature and humidity especially at early ages, grade, fineness and proportions of GGBS, composition of OPC etc. The effects of fineness, curing regime and replacement level have already been discussed in the earlier topics. For a given proportion of GGBS the percentage increase in the strength, as compared to that of OPC concrete, increases with increasing water to cementitious material ratio [Meusel and Rose, 1983].

The sensitiveness of GGBS concrete to the curing conditions poses a problem in practical construction works especially for thicker sections. It has been found that the in-place strength of concrete with GGBS blends is significantly less than the standard cured cylinders (bath-curing at 23 °C), and sealed curing is the most representative of the in-place curing conditions [Sanjayan and Sioulas, 2000]. This is especially pertinent to large high-strength concrete elements. It was observed by Sanjayan and Sioulas that the ratio of compressive strength of cores taken from in-place cast columns to that of standard bath-cured cylinders containing GGBS was significantly lower than 0.85, a typical value assumed in design, and the degree of overestimation was exacerbated with increasing slag content.

Again results of studies on flexural strength show that, when comparisons are made on the basis of equal compressive strength, the modulus of rupture of GGBS concrete is the same or slightly lower than that of OPC concrete at very early ages. But,

at 7 and 28 days slag concrete has a higher and some times significantly higher flexural strength than OPC concrete [Malhotra, 1980, & Hogan and Meusel, 1981]. The superior flexural strength of slag concrete (for equal compressive strength) is more noticeable in the case of higher strength mixes in which the flexural strength may exceed that of OPC concrete by as much as 16 percent. The higher modulus of rupture at ages beyond 7 days is believed to be due to the increased denseness of the concrete matrix.

2.6.4 Modulus of elasticity:

Most of the work in this field has been done on blended cements containing slag. A PCI investigation carried out to compare the elastic properties of OPC and slag concretes showed that on the basis of equal compressive strengths at 28 days, there appears to be little difference between the two types of cement. However, concrete with blends more than 50% slag, may give elastic modulus results slightly lower than that OPC concrete. JSCE subcommittee report [1986] suggests a value 1.4×10^5 kgf/cm², for designing a structure using working stress method or for calculating stresses.

2.6.5 Creep and drying shrinkage:

There is very limited data available on creep and shrinkage of concrete containing GGBS, and this limited data indicate towards conflicting results. While some investigators believe that the creep and shrinkage strains are generally greater in the case of GGBS blends [Fluton, 1974; Hogan and Meusel, 1981], some other believe that for similar compressive strength, these values are of similar magnitude when compared to OPC concrete [Swamy, 1999]. The creep and shrinkage in a concrete mainly depends on curing history of slag concrete. Inadequate and improper curing of these concretes lead to higher amount of creep and shrinkage strains. In order to decrease the drying shrinkage and creep of slag concrete, sufficient moist curing and relatively low water/cementitious ratio are required.

2.6.6 Autogenous shrinkage

Autogenous shrinkage of concrete is the shrinkage that occurs at constant temperature, without any moisture movement between the concrete specimen and the environment. It is caused by self-desiccation as a result of water consumption in hydration of cementitious materials. The mechanism of capillary pore pressure used to explain the drying shrinkage of concrete is also applicable to autogenous shrinkage, the only difference is in the cause of moisture loss. In ordinary concrete the autogenous shrinkage is very small and is often neglected, but High Performance concrete (HPC) is prone to large autogenous shrinkage due to presence of large amount of cementitious material [Lim and Wee, 2000]. And with the use of GGBS or Silica Fume it is aggravated due to refinement of pores resulting in greater capillary pressure.

Test data on autogenous shrinkage of concrete incorporating GGBS are limited, yet the literature and investigation reported by Lim and Wee shows that its use could significantly increase the autogenous shrinkage, especially in the case of HPC, leading to cracking even in the absence of drying. It was also observed that a GGBS replacement level of 50% had the largest autogenous shrinkage, as it should be because the compressive strength is reported to be highest at this replacement level indicating maximum hydration.

2.7 Durability of concretes incorporating GGBS

Durability of concrete is the most desirable property of concrete, especially when it is used in an aggressive environment. However, enough attention has not been given, in past, to design for durability and strength and workability of concrete mix had been the main guiding factors. But recently the importance of durability and the need to design for it has been recognised.

Presently concrete has become the most widely used construction material, and is being used in all type of environments and ambient conditions. However, when it is to be used in an aggressive environment, proper selection of concrete making materials is of critical importance. Selection of improper concrete ingredients may lead to serious deterioration due to physical and chemical actions. The available data on use of slag, and experiences from practical applications clearly show that the durability of concrete can be significantly improved by incorporating GGBS in concrete. This greatly enhanced durability is primarily due to: lower heat of hydration, continued pozzolanic reaction, and highly improved pore structure. The different aspects of durability of GGBS concrete are discussed in brief, below.

2.7.1 Permeability

The porosity and permeability of concrete is probably the most important parameter influencing both the strength and durability. Concretes having lower permeability physically resist the ingress of aggressive ions such as chlorides and sulphates and that of gases like carbon dioxide. The permeability of matured concretes containing GGBS is reported to be significantly lower than that of OPC concretes, and the permeability decreases as the slag content is increased. It has been found that, the pore structure of cementitious matrix of GGBS concretes is changed through the continued reaction of slag with the calcium hydroxide and alkalis released during the Portland cement hydration. Normally, permeability of concrete depends on its porosity and pore-size distribution. Using mercury insertion techniques, several investigations have shown that incorporation of GGBS in cement paste helps in the transformation of large pores in the paste into smaller pores, resulting in decreased permeability of the matrix.

2.7.2 Resistance to alkali-aggregate reaction (AAR)

The ability of GGBS to reduce or even prevent expansion due to AAR is well established from numerous laboratory investigations and from experience of actual structures. As reported by Nishibayashi et al [1995], the expansion due to alkali aggregate reactions can be greatly reduced by using blended cement. He adds that promising results are obtained by using 50% or more slag in the binder. This ability of GGBS is attributed to its strong stabilising effect on the alkali-ions, and also to the alkali-dilution effect produced by it. The above-mentioned view is supported by many other investigators like Hogan [1983], Higgins [1995], and Wang et al [1995].

In many countries use of GGBS is a specified measure for reducing expansion due to alkali-silica reaction in concrete. It is proposed that slag can adsorb some alkali metal ions on its surface due to its capacity to combine with them, this property of GGBS hydrates can be explained on the basis that the CSH gel in GGBS concrete contain lesser amount of calcium. Thus the concentration of alkali ions in pore solution is reduced. Also, the microstructure of hardened slag-cement concrete matrix is denser as compared to that of OPC concrete, leading to decreased rate of diffusion of the alkali ions. According to appendix of ASTM - C: 989, where GGBS is used in quantities greater than 40% of the total cementitious material, reduced expansion due to ASR is found with cement having alkali contents up to 1.0%. Some investigators report that where slag contents are used in percentages from 40 to 65 of total cementitious material, expansion is virtually eliminated.

2.7.3 Resistance against freeze and thaw

The durability of concrete to repeated freezing and thawing cycles is important in cold regions, where sub-zero temperatures are encountered in winter season. The available literature shows that the concrete incorporating GGBS or Silica Fume

generally have higher resistance to freeze-thaw cycles. Virtanen [1983] observed that 1) air content of concrete has the greatest influence on the Freeze-thaw resistance of concrete 2) additives like GGBS, Fly-ash and Silica-fume require higher doses of air entraining admixtures to reach a certain air content & 3) addition of GGBS resulted in slight improvement in the freeze-thaw resistance of concrete, when strength and air content are kept constant. Whereas Pigeon and Regourd [1983], did not find any significant difference in the freeze-thaw resistance of GGBS and OPC concrete and suggested further studies on them. Nakamoto et al [1998], write that air-entrained concrete having slag content upto 70% show comparable or superior freeze-thaw resistance, but if we further increase the slag content then the performance is reduced. However, by using air-entraining high-range water-reducing admixtures we can get good resistance against freezing and thawing even in the case of slag replacements upto 95%.

2.7.4 Resistance to sulfate attack

Sulfate attack is a major problem in aggressive environments, i.e. when concrete is exposed to seawater or ground water containing sulfate. Sulfate salts such as Na_2SO_4 , MgSO_4 and CaSO_4 penetrate into concrete and react with:

- (i) Calcium hydroxide (CH) to form Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which has a volume 1.24 times greater than that of CH.
- (ii) Hydrated Aluminates, forming mono and tri sulphoaluminates, known as ettringite, having 2.5 times more volume than that of original aluminates.
- (iii) Hardened C-S-H matrix, causing decomposition of the C-S-H and softening of the matrix.

The last reaction is favoured by low pH, i.e. lower amount of CH and by the

presence of Mg^{2+} ions. So, entrigite formation is dominant effect if Al_2O_3 and CH are present in abundance. But in the case of blended cements, specially with GGBS, CH content is low and hence the latter process of weakening of C-S-H matrix and loss of adhesion appear to be at least as important in practice as expansion and cracking due to increase in volume.

There is extensive text evidence to show that slag concrete has excellent resistance to sulfate attack. The increased resistance to sulfate attack in concrete incorporating GGBS has been acknowledged by all major European codes of practice. When the replacement level of GGBS is 70% then the blended cement were found to have superior resistance than Sulfate-Resisting Portland Cement [Swamy, 1999]. The sulfate resistance is seen to increase with increasing proportions of GGBS. Although water-binder ratio is an important parameter in controlling sulfate resistance, at higher replacement levels the slag content is seen to be more influential than the water-binder ratio [Frearson, 1986]. But, to ensure good service-life and resistance against sulfate attack, high replacements levels of 70% and low water-binder ratio of 0.45 are recommended [Frearson, 1992].

Studies conducted on GGBS at Holderbank, Italy indicate that concrete made with 50% GGBS has on average 65% lower expansion due to sulfate attack than that of OPC concrete. But Mehta [1992], concluded that though much attention has been paid to expansion and cracking as the damaging effect of sulfate attack, in the case of GGBS concrete the field experience has shown that loss of adhesion and strength are normally more important.

2.7.5 Effect on rate of carbonation

Carbonation of concretes incorporating supplementary cementitious materials has raised concern on use of these materials to prevent corrosion of reinforcement. This

concern has been raised due to realization of the fact that a lot of CH produced during hydration of cement is consumed in the later pozzolanic reactions. It is more concerning in the case of GGBS incorporation because of higher replacements of plain cement in this case. However, in considering carbonation rate, the two opposing effects, i.e. the reduced buffer capacity of pore solution of GGBS incorporating concretes and the decreased permeability of concrete due to pore refinement, must be taken into consideration

It is generally agreed that incorporation of GGBS or other mineral admixtures causes an increase in carbonation rate of concretes. Adolf Mayer [1986], conducted extensive studies on carbonation of slag concretes. He found that, the depth of carbonation increased with an increasing percentage of slag. At 50% of slag replacement level, the carbonation was 1.5 times as deep as in OPC concrete, while it was 2 times as deep, when the percentage of slag was 70%. He further observed that the rate of carbonation also depends on the age of concrete and water/cementitious ratio. The duration of moist curing also plays important role in carbonation of slag concretes.

Osborne [1989], conducted studies on carbonation and permeability of blast furnace slag concretes from field structures. He observed that concrete blocks with low cement content (250 kg/m^3) and high slag replacement level were particularly susceptible to high rate of carbonation. With increase in the cement content and reduction in the slag percentage the carbonation reduced substantially. He further observes that concretes with a total cement content of 450 kg/m^3 showed very low depth of carbonation even at 70% replacement by slag.

Nakamoto and Togawa [1995] also carried out studies on large number of specimens to study strength development and carbonation of concretes incorporating high volumes of blast furnace slag. The slag replacement level was varied from 50% to 95% by weight

and the fineness of slag was varied from 4000 to 8000 cm^2/g . They observed that the rate of carbonation increased with increase in slag content, especially at higher water/cementitious ratios. However, the increase was not very high for 50% cement replacement. The rate of carbonation showed a much faster increase when the cement replacement by slag increased above 70%. The results of carbonation depth as a function of square root of time as obtained by the authors have been given in the Figure 2.7 for different replacement levels. The authors also observed that the increase in the fineness of slag was effective in lowering the rate of carbonation. They further state that the period of water curing before the carbonation test also affects the rate of carbonation and for checking rate of carbonation, sufficient moist curing should be given to concretes incorporating higher volumes of slag.

Nakamoto and Togawa further observed that, similar to the OPC concretes, the depth of carbonation of high volume blast-furnace slag concrete is also proportional to the square root of time, which is evident from Figure 2.7, and using this relationship the progress of carbonation in field exposure can be calculated. They also tried to relate strength development and carbonation rate and found that rate of carbonation is proportional to the reciprocal of strength in all concretes, but the relation is strongly influenced by the period of water curing.

2.7.6 Effect on penetration of chloride ions

It has long been recognized that the use of cement containing granulated slag or pozzolanic admixtures is effective in reducing the penetration of chloride in cement pastes, mortars, and concretes. This reduction has been ascribed to blended cement pastes having a more refined pore structure, reduced permeability, and an increased capacity to bind chloride ions.

In a study reported by D. M. Roy [1989], in which he studies chloride diffusion of cement pastes and mortars incorporating separately ground slag, using rapid chloride permeability test (AASHTO-227), it was observed that higher slag replacement levels significantly decrease the transport rate of chlorides. The data clearly show a many fold drop in charge passage by 50% replacement of cement of cement by slag. The pronounced decrease in chloride is related to the refined microstructure. It was observed that the pore structure of hardened slag-containing pastes was dominated by pores with radius finer than 5 nm, whereas in OPC pastes the majority pores range from 5-20 nm.

Another study conducted by Swamy and Laiw [1995], also reports similar results. They compared the effectiveness of supplementary cementing materials in controlling chloride penetration into concrete, by performing natural diffusion tests for 18 months. Higher water/binder ratios (0.6 & 0.75) were deliberately used to accelerate the penetration of chlorides. It was observed that all cement replacement material, i.e. 65% slag, 30% fly ash, or 10% silica fume, reduced both the depth of penetration and the chloride concentration at a given depth from the concrete surface. It is also reported that silica fume was most effective and fly ash was least. Slag was effective in resisting chloride penetration even at a water/binder ratio of 0.75 and showed consistently lower concentrations for all exposure conditions upto 50 cycles.

Increased resistance to chloride penetration due to addition of slag has also been reported by Polder [1996]. He also reports of the field examples where blast furnace slag has been used in high replacement levels to enhance chloride penetration resistance in Netherlands for many decades. Osborne [1992], also indicates of similar results in his study. He observes that the ingress of chloride was reduced as the percentage of slag used as replacement for OPC was increased, i.e. there was least chloride present at 21mm depth for concretes containing 80% slag.

Streicher et al [1995], studied diffusivity changes of different cements due to presence of chloride ions. They inform that a number of researchers have identified a change in concrete microstructure and pore system due to presence of chloride ions, but they disagree on the exact mechanism involved in this change. The authors observed in their study that the chloride conductivity of a range of concrete mixes reduced significantly with time (over two weeks period) when immersed in a 5M NaCl solution. This reduction of conductivity was higher for blended cements and was greatest for GGBS, as can be interpreted from the Figure 2.9. The ability of GGBS to reduce chloride diffusion was also apparent in their study as can be interpreted seeing the lowest chloride conductivities shown by them. It is suggested that this reduction is mainly due to a change in the physical pore structure affecting the diffusivity of the material. Though the exact mechanism is not known, yet researchers have suggested that formation of calcium chloride on the surface of CSH or a change in the hydroxyl of the CSH gel occurs in the presence of chloride ions.

Thomas et al [1999] conducted long term studies on the effect of fly ash and slag incorporation on transfer properties of concrete. They observed that the effect of fly ash and slag on mass transfer properties of concrete has been well documented. However, much of the available data relatively short term testing, i.e. one month to one year. They further observed that results of few long term studies show that incorporation of these admixtures have little impact on transfer properties determined at early ages, but can lead to order of magnitude improvements in long term. Rate of chloride penetration during first six months is not much different for concretes with or without mineral admixtures. However, after a few years there is dramatic decrease in chloride ingress rate. They observed in their study that slag concretes, with a replacement level of 70 % have a much higher diffusion coefficient at early ages (e.g. ≤ 28 days) compared with

OPC or Fly ash concretes. However, the diffusion coefficient decreased rapidly with time. A long-term data on Diffusion Coefficients (D_a) and Surface Concentration (C_s) values have been provided by the authors, for three types of concrete mixes, i.e. OPC mix (PC), 70 %OPC + 30 fly ash mix (PFA), 30%OPC + 70% slag mix (PGBS). The same data is being provided here also.

Age	$D_a \times 10^{12} \text{ m}^2/\text{s}$			C_s (as % of concrete)		
	PC	PFA	PGBS	PC	PFA	PGBS
6 months	9.5	4.3	7.5	0.35	0.42	0.58
1 year	3.0	2.0	2.9	0.69	0.53	0.68
2 year	7.6	1.9	1.9	0.38	0.45	0.46
3 year	5.6	1.1	0.99	0.42	0.54	0.54
6 year	10	0.81	1.0	0.28	0.48	0.46
8 year	8.7	0.59	0.63	0.31	0.56	0.48

Based on their 8 year long study of chloride diffusion Thomas et al developed a comprehensive chloride penetration model in which they took diffusion coefficient as a function of time and denoted it as

$$D_t = D_{28} \left(\frac{28}{t} \right)^m$$

Where, D_t = diffusion coefficient at time t in days.

D_{28} = diffusion coefficient at 28 day age

And, m = constant.

From their experimental study and regression analysis, they obtained the values of ' m ' as 0.1, 0.7, and 1.2 for OPC, fly ash, and slag respectively. This shows that improvement in diffusion resistance with time is faster in case of slag. The values of C_s , D_{28} and m as obtained by Thomas et al are given below in a tabular form.

	OPC	Fly ash (30%)	Slag (70%)
C_s (%)	0.35	0.50	0.50
D_{28} (m^2/s)	8×10^{-12}	6×10^{-12}	2.5×10^{-11}
M	0.1	0.7	1.2

As per the studies conducted at National Council for Cement and Building Materials (NCB), New Delhi, India, the chloride diffusivity is substantially reduced in the case of GGBS concrete compared to that of OPC and Sulphate Resisting Cement (SRC) Concretes [Prasad & Babu, 1999]. Short and page [1982], have reported the diffusion of chloride ions into Portland and blended cement pastes and have found the following values of diffusion coefficients for different cement types.

Type of Cement	Diffusivity ($\times 10^{-9} \text{ cm}^2/\text{s}$)
SRC	100
OPC	44.7
Fly ash + OPC	14.7
50% OPC + 50% GGBS	4.1

Therefore, we see that there is many fold decrease in the diffusivity of chloride ions into pastes incorporating GGBS, but they did not mention, at what age of the cement pastes they got these values.

2.8 Concluding remarks:

GGBS have considerable potential as a partial replacement for Portland cement, especially for enhancing the durability of concrete structures. The proportions of replacement can be decided depending upon the intended use and exposure conditions. The effect of lower ambient temperature on the hydration of GGBS+OPC system should

be taken into consideration in winter concreting. Also, proper and slightly prolonged curing should be done while using GGBS, seeing its higher susceptibility to curing and to avoid shrinkage cracks at early ages

In spite of a general acceptance of greater durability potential of GGBS incorporating concretes, contradictory results have sometimes been reported. Therefore, more research is needed to develop more thorough and long-term data on mechanical properties and durability of concretes incorporating GGBS. These studies are especially required on creep and shrinkage of GGBS concretes from mechanical properties point of view and on chloride penetration, carbonation, and threshold chloride level for durability point of view.

With this in mind, present study has been undertaken. Lot of work has been done on modeling and predicting chloride penetration in OPC concretes. Studies have also been conducted on GGBS incorporating concretes, for comparing their resistance to chloride penetration to that of OPC concretes, which give a general information that use of GGBS in concrete potentially decreases chloride penetration. Using rapid chloride permeability test, which uses electric field for accelerating the rate of chloride penetration, has done most of these studies, which certainly give a relative measure of diffusivity, but actual diffusivity calculated from these may not be realistic. This information are not sufficient for developing realistic models for predicting future chloride penetration, due to the complexity of the chloride penetration phenomenon and its dependence on a variety of factors. Moreover, there is a lack of long-term data in this field. In present programme an attempt has been made for providing more of the required data and creating a basis for development of some model for predicting chloride penetration of concretes incorporating GGBS. However, the chloride penetration studies could be conducted for 6 months only due to the period of the programme.

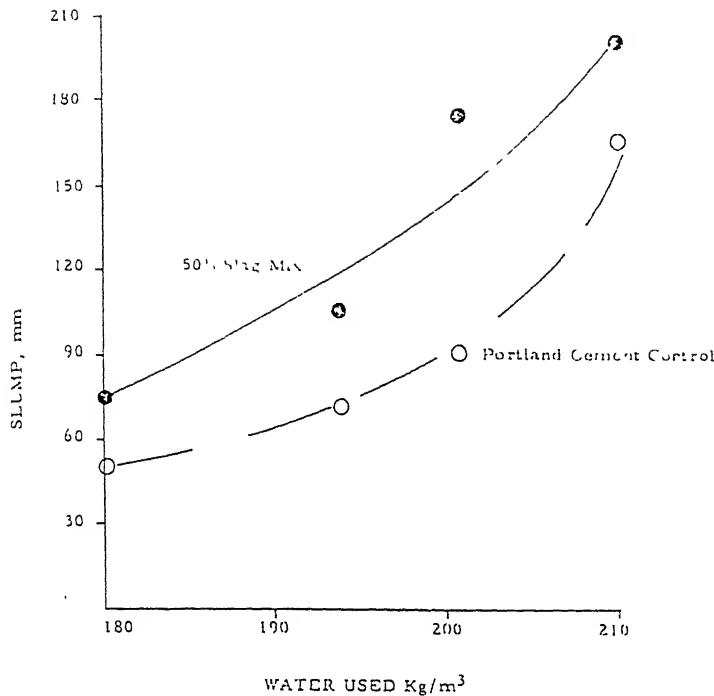


Figure 2.1: Slump comparison of slag concrete verses Portland cement control
[Meusel and Rose, 1983]

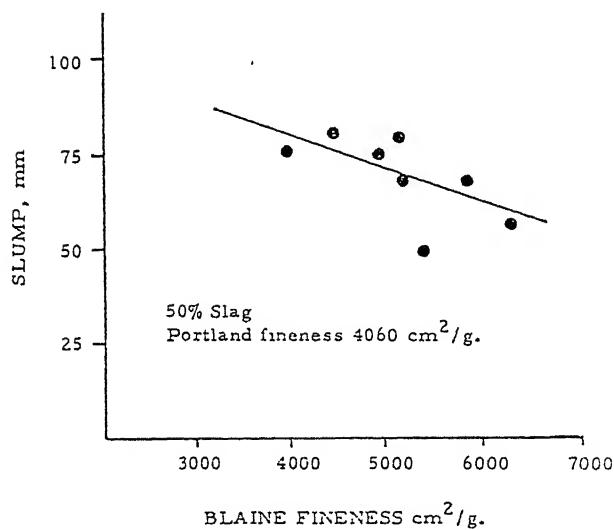
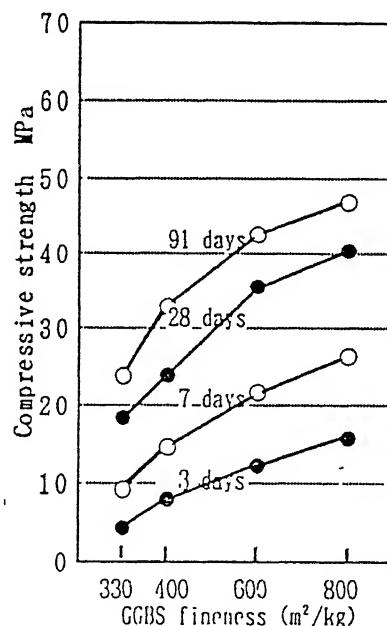
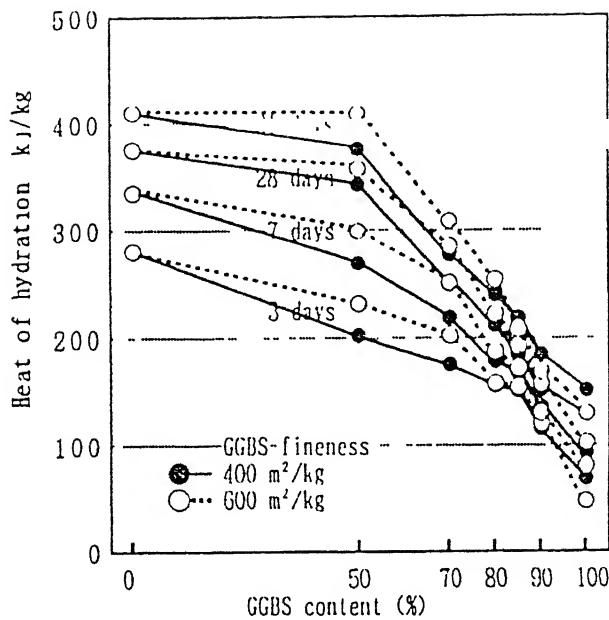


Figure 2.2: Effect of slag fineness on workability of concrete
[Meusel and Rose, 1983]



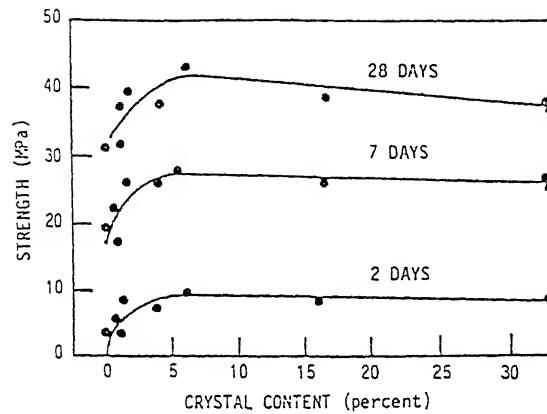


Figure 2.5: Relationship between crystal content of GGBS and strength development of standard ISO mortars (76% slag, 19% clinker, 55 gypsum)
 [Hootan and Emery, 1983]

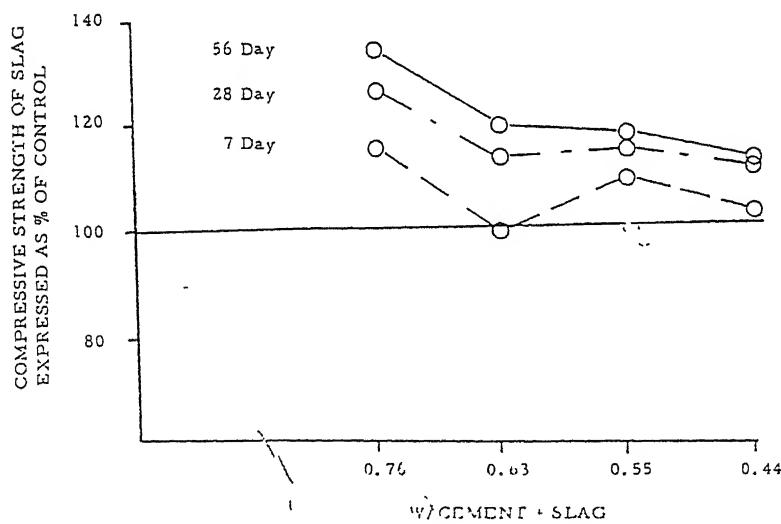


Figure 2.6: Relationship between W/B ratio and compressive strength of slag concrete expressed as percentage of control
 [Meusel and Rose, 1983]

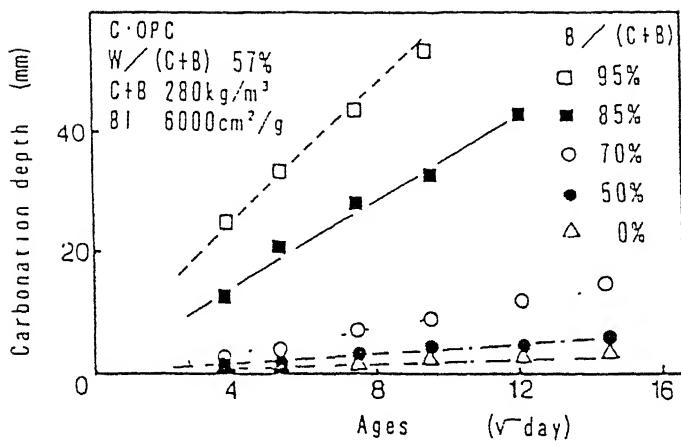


Figure 2.7: Progress of carbonation in GGBS concretes (accelerated tests)
[Nakamoto and Togawa, 1995]

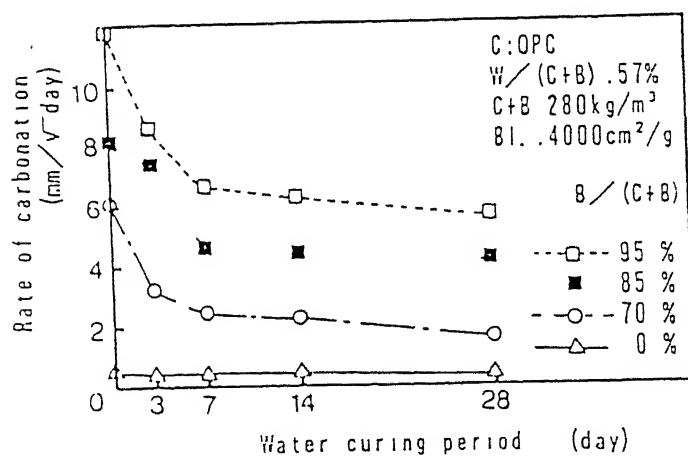


Figure 2.8: Relationship between rate of carbonation and water-curing period
[Nakamoto and Togawa, 1995]

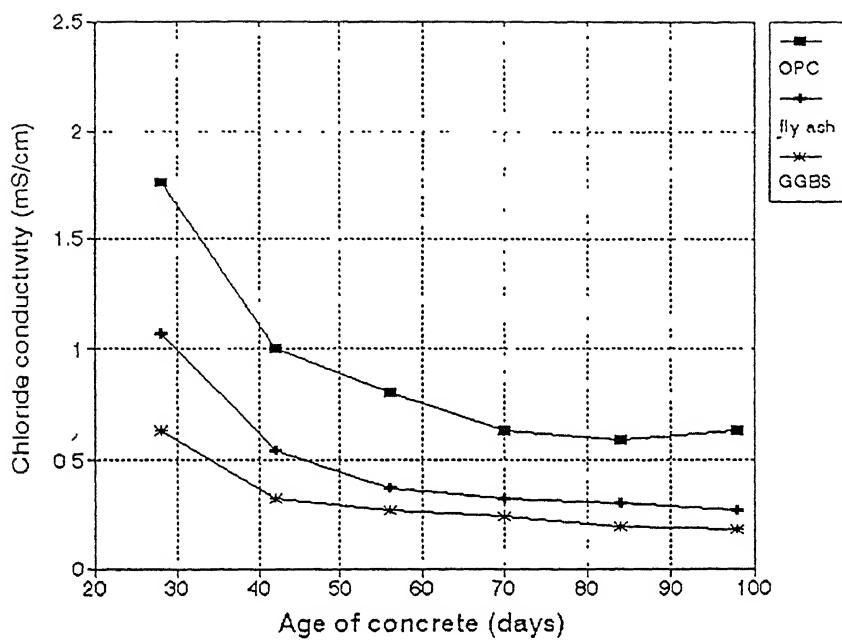


Figure 2.9: Reduction in chloride conductivity after immersion in chloride solution at 28 days

[Streicher and Alexander, 1995]

Chapter 3

CHLORIDE PENETRATION IN CONCRETE

3.1 Introduction

Concrete can be exposed to chloride attack in marine environment, where seawater contains large amount of dissolved salts, predominantly sodium chloride. Other sources of chloride include use of sea-sand and water in concrete construction, deicing salts used in cold regions to melt away snow on highways etc., and some times ground water containing chloride salts.

3.2 Mechanism of chloride penetration

In all the cases mentioned above, chloride (ions) that appears at the surface of concrete 'migrate' inside and concentrates within the concrete. This chloride penetration in concrete is a very complicated process; involving many material properties such as diffusivity, binding capacity, pore solution chemistry etc, as well as different physical modes of penetration such as permeation of salt solution, capillary absorption of salt solution and/or migration of chloride ions through diffusion. It has been reported that temperature also plays a vital role in chloride penetration [Tang and Sandberg, 1996].

Further, depending upon the exposure and moisture condition of the concrete elements, the individual mechanisms of penetration may act simultaneously or individually. In moisture saturated concrete diffusion is the dominant phenomenon whereas, in dry concrete capillary absorption is more influential. Thus, under conditions of cyclic exposure to chlorides, the process (of penetration of Cl^-) is likely to be combination of both. It is so because the inner concrete remains saturated due to frequent

submersion and higher relative humidity, promoting diffusion where as, surface layer often becomes partially dry, subsequently allowing capillary absorption. But, since the capillary absorption mechanism is active only in the thin outer layer of concrete, it is the diffusivity of concrete, which has drawn more attention of the investigators.

Diffusion can be defined as the process by which matter is transported from one part of system to another as a result of random molecular motion. In this phenomenon though there is no preferred direction of motion of any particular molecule, yet on an average the transfer takes place from a region of higher concentration to that of lower concentration.

Recognizing the analogy of diffusion mechanism with that of heat conduction, Fick first put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived by Fourier [J. Crank]. Thus, Fick's first law states that "in an isotropic medium the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section. i.e.

$$J = -D \frac{\partial C}{\partial x} \quad \dots \quad (3.1)$$

Where,

J = flux of diffusing substance

C = concentration of diffusing substance

x = space co-ordinate normal to the section

and, D = diffusion coefficient

The above equation (3.1) and 'its' solution can be given as below.

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \quad \dots \quad (3.2)$$

The equation (3.2) is referred to as Fick's second law, which is widely used for mathematical modeling of chloride diffusion in concrete. In order to be able to predict

chloride penetration in concrete, without having to carry out explicit experiments, several researchers have modeled the problem as simple a one-dimensional diffusion, and attempted to apply the Fick's equations. Now, though the details of the derivation of the diffusion equation are given in the Appendix [1], the solution, predicting the concentration at a location 'x' below the (outside) surface at a time 't' after the exposure is given below.

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad \text{----- (3.3)}$$

Where, $\operatorname{erf}(z)$ is the standard error function, given as:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$

It is a standard mathematical function and extensive tables of it are available.

Before getting involved in a detailed discussion on the above equation, it is important to understand that whereas the Fickian diffusion model holds essentially for a non-reactive medium, the assumption is only partly valid in the case of chloride diffusion in concrete. It is well known that certain hydration products, especially those of tricalcium aluminate, combine with chloride to form 'Freidel's salt', though the extent of such a reaction and the limiting value of the chloride binding is not clearly known.

Further, it can be seen that the Fickian formulation uses two important parameters, D and C_s . An effort has been made in this section to put in perspective these two parameters in the context of chloride diffusion in concrete. It may be mentioned here that more often than not, the Fickian one-dimensional simplification is used more by way of a necessity in the absence of better and equally simple tools than because it accurately represents the process of chloride diffusion in concrete.

3.2.1 The diffusion coefficient 'D'

The Fickian model, explained in the Appendix, is based on the assumption that the diffusion coefficient is constant over time (and also independent of x). Now in the case of concrete perhaps neither is strictly valid. It is known that the hydration of concrete continues for a long period of time and thereby the 'porosity' (which is at the root of the diffusion process) and therefore the diffusion coefficient, is indeed really a function of time. Thus, any estimate of the diffusion coefficient is only an average over the time over which the exposure is carried out.

It should be noted that to keep the effect of the changes in the D over time to as small as possible, all specimens were cured in water for an initial period of 4 weeks, before exposure to the chloride environment.

It has already been mentioned earlier that any estimate of the diffusion coefficient is only an average over the time over which the exposure is carried out. Thus, when the value is evaluated using the chloride concentration profile obtained at the end of the 6 week (or any other duration) exposure, what we really get is the average diffusion coefficient obtained over that time period. In all fairness it should be borne in mind that in view of the difficulties in adapting the known diffusion model to represent the chloride penetration in concrete, the diffusion coefficient is often referred to as the 'apparent' coefficient of diffusion and suffixed with an '*app*' after the D .

3.2.2 Pseudo-equilibrium constant ' C_S '

So far as the pseudo-equilibrium constant C_S is concerned, it really represents the *constant concentration at the surface (i.e. at $x=0$, for all t)*. In the context of the present problem it can be best understood as an equilibrium concentration of chlorides in a narrow 'slice' of concrete near the surface. In fact, even this assumes the existence of a

limiting amount of chlorides that can be held in a certain volume (or mass) of concrete – no matter what the mechanism of chloride binding is.

Now, it should be noted that since the concrete does not contain practically any chloride at the time of start of chloride exposure, it could take some time before this '*equilibrium concentration*' in the layers near the surface is achieved. This is clearly brought out by the fact that the chloride concentration obtained near the surface at the end of the initial 6 week exposure (any mix) is much lower than that obtained at the end of the 6 month exposure. Needless to say, the same trend is established from the best fit of the data carried out later.

3.3 Measurements and prediction of diffusion coefficient of concrete

Measurement of diffusion coefficient and permeability of concrete, mathematical modeling of these phenomena and, their prediction is very important for better understand the durability of concrete structures susceptible to reinforcement corrosion. Therefore, extensive work has been done in this field of concrete technology. The greatest problem with the conventional methods used to measure these transport properties is that, they are very time consuming, labour-intensive and, often give inconsistent results due to non-homogeneity of concrete. But then, they are most near the natural exposure conditions and take into account actual process of diffusion and permeation, as it happens actually in practice. These methods generally use the Fick's laws of diffusion for modeling the diffusion phenomenon. There are also some accelerated tests which use electric field to accelerate the transport of chloride ions., and Nernst-Plank equation can be used for computing diffusion coefficients from the measurements of these tests. There have also been some recent developments, which use modern techniques such as 'impedance spectroscopy', 'nuclear magnetic resonance' etc.

for measuring the transport properties of matter. The information from these tests are used to predict transport properties using Nernst-Einstein equation (diffusivity) and Katz-Thompson equation (permeability) [Shane et al, 1995]. Some relevant existing and emerging techniques for measuring or predicting diffusivity of concrete are discussed under this sub-topic.

3.3.1 Conventional techniques

3.3.1.1 Conventional and concentrated immersion/ponding test

In conventional immersion test, natural exposure condition is simulated by immersing the concrete specimens in NaCl solutions for a specified duration. The change in the concentration of chloride ions with respect to depth of penetration is determined by drilling the specimen and titrating the collected powder. Finally diffusion coefficient is found by fitting the concentration profile with the developed models based on Fick's laws. Concentrated immersion test is also similar to conventional immersion test but for a highly increased concentration of immersion solution (3-5 M NaCl), used to accelerate the diffusion process [Tang & Nilsson, 1995]. The test is well described in a Danish Standard APM-302.

In general the diffusion coefficient takes into account the total chloride entering the concrete specimen. But, if we consider the binding of chloride with the concrete microstructure, i.e. only free chloride present in pore solution is taken for profiling, the coefficient calculated is known as apparent diffusion coefficient.

The biggest limitation of ponding test is that it is very time consuming. Requirement of longer time of exposure also restrict the test to the measurement of diffusivity of the matured pastes, mortars and concretes only.

3.3.1.2 Divided diffusion cell

In this method a disk-shaped specimen is placed between two ionic solutions, one of which is reservoir containing alkaline chloride solution ($\text{NaOH} + \text{NaCl}$), and other is sink containing hydroxide solution (NaOH). Hydroxide solution (NaOH) is used in both compartments to reduce leaching of $\text{Ca}(\text{OH})_2$. The Cl^- ion concentration of the reservoir is kept constant. When steady state is reached, i.e. there is no chloride bounding and all chloride entering the disk passes to the sink, then the effective diffusion coefficient can then be calculated as:

$$D_{\text{eff}} = \frac{\Delta Q / At}{(C_a - C_b) / L}$$
$$\Rightarrow D_{\text{eff}} = \frac{\Delta QL}{(C_a - C_b)At}$$

Where, ΔQ = change in chloride content of the sink, in time 't';

L = thickness of disk-shaped specimen;

A = area of the disk-shaped specimen;

C_a = chloride concentration in reservoir;

C_b = mean chloride concentration in the sink, over time 't';

Tang and Nilsson, 1992, report that the actual chloride concentration gradient in the diffusion cell is lower than that obtained simply from the bulk solution.

i.e. $(C_{\text{Sa}} - C_{\text{Sb}}) < (C_a - C_b)$

They obtained concentration profiles, as shown in Figure (3.1), using chloride-selective electrodes at different places in diffusion cell.

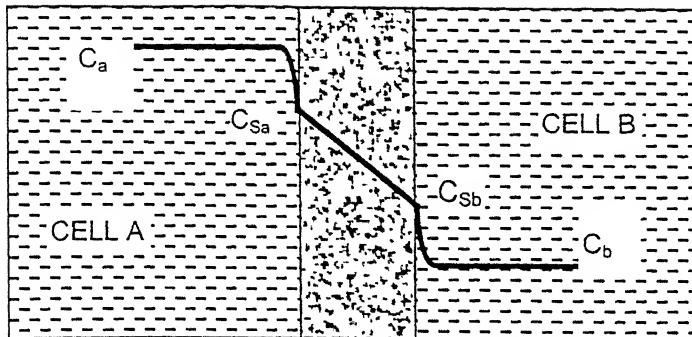


Figure 3.1. Chloride concentration distribution in diffusion cell

The draw back of this test is again the time required to perform the test and to reach the steady state, which limits the test to matured specimens only.

3.3.1.3 *Rapid chloride migration test*

This test, which is generally referred as rapid chloride permeability test, was developed by D. Whiting. The test has been adopted by AASHTO-T277:83 and ASTM-C1202:91 as a standard test method for finding relative diffusivities of concretes and mortars. The test became popular because it dramatically shortened the time required for the diffusivity test (i.e.6 hours) The test setup is similar to Diffusion-Cell, with an additional application of strong electric field to accelerate the movement of ions through the concrete disk. The reservoir filled with NaCl solution contains anode and that filled with NaOH contains cathode. The total charge passing through the disk over certain duration is measured and is related to the chloride diffusivity. The test defines that a higher amount of coulombs represents a higher permeability of concrete to chlorides.

Though this test is very fast, but it also have its limitations. Firstly, the test does not give the actual diffusion coefficient of the specimen, but only qualitative or comparative measure of diffusivity. The application of a high D.C. voltage (60 V) may result in heating of specimen, if the specimens are more permeable (low resistivity). This may have a profound effect on the diffusion coefficient. Moreover, the test also induces

changes in pore structure, pore solution chemistry and, resistivity of the concrete specimens [Feldman et al, 1994].

In a critical review of this test method, by C. Andrade, 1993, it has been observed that the rapid chloride permeability test contains some significant errors and uncertainties, such as:

- i) When electric field is applied across the concrete disk (specimen), migration of all ions occurs towards the opposite sign electrode, i.e. it is not only chloride ions which is moving, but all the ions move. Therefore, it accounts the total current corresponding to all ions and not only that corresponding to chloride ion flow.
- ii) The high voltage drop (60 V), used in the test, induces joules heating, which in turn changes the transport characteristic of concrete.

In a study on 'chloride diffusion of slag cement pastes and mortars' reported by D. M. Roy, 1989, in which he used this test for measuring relative diffusivity, it is mentioned that the experiments were concluded if the temperature rose to 90°C , before the 6 hour duration of the test. This means that temperature rise during this test may be as high as to reach the boiling point of water. But, he further observes that the chemical analysis of solutions in the anode and cathode compartments showed a general proportionality between the concentration of chloride ions migrated and quantity of charge passed.

So, we see that there are some uncertainties about the reliability of the test results obtained using Rapid Chloride Permeability test, none the less, owing to its speed and simplicity, the test has been increasingly used to define and predict transport characteristics of concretes and mortars, specially pertaining to chloride penetration.

3.3.1.4 Modified rapid chloride migration test (Norwegian test)

This test was designed to correct some of the shortcomings of the rapid chloride permeability test [Detwiler et al, 1991]. There are two modifications in this test. Firstly, the applied voltage was decreased from 60 V to 12 V to avoid heating of specimen. The lowering of applied electric field increased significantly the time required for the test. Secondly, instead of measuring charge passing through the specimen, the chloride concentration in the NaOH solution was monitored periodically for the duration of the test. As stated by Detwiler et al this data can be used to calculate diffusion coefficient but the solution is very difficult. They obtained a bilinear curve for the plot of concentration against time. They further observe that, diffusion coefficient is a function of potential difference as well as concentration gradient.

There is no fixed duration for the test as there is in the rapid chloride permeability test. This test is also an steady state test, and to reach steady state the test can take anywhere from few days to few week, depending upon the diffusivity of the specimen. The test requires constant monitoring of the apparatus and chloride concentration in the compartments of the diffusion cell. So, there are several limitations of this test also from a practical point of view.

3.3.1.5 Non-steady state migration test

The first non-steady state migration test, to determine the diffusion coefficient of concrete was proposed by Tang and Nilsson in 1992. The test was developed keeping in mind the inability of Whiting's test to directly give chloride diffusivity, i.e. it was aimed to directly and rapidly determine the chloride diffusivity of concrete. The test involves applying a potential of 30 V, instead of 60 V of Whiting's test, across a 50 mm thick specimen for certain duration, i.e. a few hours or days. Then the specimen is split into

two pieces and the penetration depth of chloride is measured by using a colorimetric method. The chloride content at different depths can also be determined by slicing the split specimen, grinding it and then, titrating it with 0.01 N AgNO_3 solution. However, the reading used to determine the diffusion coefficient is the penetration depth of chloride. Tang published further developments in the analytical part of the test in 1995.

3.3.2 Developments using modern techniques

A number of special techniques have recently emerged that have potential of measuring or predicting the transport properties of matter in an efficient way. During the past two decades or so, significant progress has been made in the related area of diffusivity and permeability of sedimentary rocks and, in relating these coefficients to the pore structure. These newer concepts of transport in porous media can be applied to ascertain transport properties of cementitious materials also. Some of these newer techniques are given below.

3.3.2.1 Impedance spectroscopy

Impedance Spectroscopy is an experimental technique that is becoming increasingly prevalent in the study of materials. It involves applying an ac. excitation signal to the specimen and recording the time varying response [Shane et al, 1995]. It is an in-situ, nondestructive technique, which, unlike other methods, does not require a dried and therefore altered specimen. Its ability to test a single specimen repeatedly, without destroying it or changing its transport characteristics enables accurate monitoring of evolution of a given property over time.

Several parameters can be determined from the analysis of the impedance spectroscopy data, the most reliable of which is the resistance of the specimen. The inverse of resistivity gives the conductivity of the material. For cementitious materials,

diffusion process is taken as diffusion of ions through water filled pores. The value of 'D' reported usually is effective diffusion coefficient, which treats the porous solid as an effective continuum. In this case, value of 'D' and conductivity can be related to the pore structure parameters as:

$$D_{eff} = D_0 \phi \beta$$

$$\sigma = \sigma_0 \phi \beta$$

and therefore,

$$\frac{\sigma}{\sigma_0} = \frac{D_{eff}}{D_0} \quad (3.9)$$

Where, D_{eff} is the effective diffusivity of a given ion through the specimen;

D_0 is the intrinsic diffusivity of that ion in 100% pore solution, which is not much different to the diffusivity in pure water;

ϕ is the porosity of the specimen;

β is the connectivity of specimen, i.e. inverse of tortuosity;

σ is the conductivity of the specimen;

and, σ_0 is the conductivity of 100% pore solution;

Equation (3.9), which is referred as Nernst-Einstein Equation, can be used to determine the D_{eff} from the results obtained from Impedance Spectroscopy.

3.3.2.2 Nuclear magnetic resonance (NMR)

Nuclear Magnetic Resonance analysis of cement-based materials relies on the spin-echo relaxation from protons in the free water contained in the capillary pore network. It has been established that NMR relaxation rates are enhanced near a solid-liquid interface. So, by measuring the spin decay, after applying magnetic field and removing it, we can get information about pore size and its distribution [shane et al,

To measure D_{eff} , a pulsed NMR signal is used which give information about mean square displacement of molecules. If classical diffusion occurs, the diffusivity can be given by the relation:

$$r(t)^2 = 6 D_{eff} t$$

where, $r(t)^2$ is mean square displacement in time 't'

The technique has been successfully employed to monitor diffusion in sol-gel glasses, sandstones, and borosilicate glasses, but it still has to be exploited for study of diffusivity of cement-based materials.

3.4 Concluding remarks:

We have seen that on a broader view there are two approaches, one simulating the natural exposure conditions by simple ponding or using diffusion cell, which is much time consuming, and the other which uses electric field to accelerate the penetration, but in process may alter the transport properties. It should also be noted that while the former technique measures directly the apparent or effective diffusivities of chloride ions through the cementitious material, the later does not give diffusivity of chloride directly but an indirect indication of it through migration and current measurements.

So, it seems that the conventional immersion diffusion test, though much time consuming, is more reliable for predicting durability of reinforced concrete against attack of chloride containing water or solutions. However, Tang and Nilsson, 1995, found good correlation between natural non-steady state diffusion coefficients and that obtained from their model, especially at higher exposure concentrations.

It can also be observed from literature that the D_{eff} obtained in steady-state migration is usually one order higher than D_{app} values obtained from non-steady state

condition, which is obviously due to chloride binding effect in non-steady state flow. For predictive purposes in real conditions, D_{app} give better results.

Though the conventional tests are more reliable, accelerated tests are also important due to their ability to give a qualitative account of diffusivity in dramatically shortened time. But, care should be taken while extrapolating the migration experiments to natural diffusion experiments, and it can be ascertained by conducting parallel migration and diffusion experiments only, that whether migration tests model real diffusion conditions.

Further, since 'D' is actually not a constant and is a function of many parameter, such as external chloride concentration and time of testing therefore, D_{eff} obtained from steady state condition does not model the real behavior. Also it can be noted that 'D' values decrease with increase in chloride concentration in migration test due to the higher ion-ion interaction. However, it is surprising that, though it is a basic principle, it is not taken into consideration and, higher and higher external chloride concentrations are proposed with misleading goal of accelerating the chloride penetration.

Chapter 4

Experimental Investigation

4.1 Introduction

As stated earlier also, the present investigation has been carried out primarily to study chloride diffusivity of concretes containing GGBS. The diffusivity of porous materials can be determined in various ways and by using different methods and modern techniques as described in the previous chapter [Section 3.6]. However, the determination of chloride diffusivity by immersion/ponding in salt solution, though time-consuming, is most near the actual exposure conditions and to some reflects the gradual changes with time that may take place in the diffusivity under natural exposure. Therefore, this study has focused on using the immersion test to ascertain the chloride diffusion properties of concrete. It is now widely accepted that the porosity of the concrete matrix plays a vital role in determining the properties of concrete such as diffusivity and compressive strength. Thus an attempt has been made in the present study to study the effect of GGBS addition on diffusivity of concrete and development of compressive strength. In other words, since a direct measure of porosity and pore size distribution was not possible, only an indirect measure could be used. The experimental programme explaining the variables and tests carried out are explained later in this chapter [Sections 4.3, 4.4 and 4.5].

4.2 Materials used:

The materials used in this study for preparation of specimens were Portland cement (OPC), ground granulated blast-furnace slag (GGBS), coarse aggregate, fine aggregate,

superplasticizer and tap water. The relevant details of all these materials are provided below and in the following tables.

4.2.1 Cement:

Commercially available ordinary Portland cement of grade C43 was used. The physical properties and the chemical composition as provided by the manufacturer of the cement used are listed in Table 4.1.

4.2.2 Ground Granulated Blast-Furnace Slag (GGBS):

Ground Granulated Blast-Furnace Slag used in this study was obtained from Andhra Cement Company, India. The origination of the GGBS used was from Vizag Steel Plant, Visakhapatnam. Since, there is no Indian standard code for use of GGBS or its production, GGBS is being produced by the Andhra Cements as per the specifications of British Standard BS: 6699: 1992. The composition and characteristics of GGBS can vary over a wide range depending upon the nature of the ore, composition of limestone used as flux, the coke consumption, the kind of iron being made, and the quenching and grinding methods. The physical properties and the chemical composition of the GGBS used are presented in the Table 4.2.

4.2.3 Coarse Aggregate:

The coarse aggregate used obtained from Tarapur, in two different size ranges. The first one had a maximum aggregate size of 20mm and minimum size of 10mm where as the other had a maximum size of 10mm. The physical properties and grading of these aggregates are given in Table 4.3.

4.2.4 Fine Aggregate:

The fine aggregate used was locally available reddish sand obtained from Badarpur. The physical properties and results from its sieve analysis results are given in Table 4.4.

4.2.5 Superplasticizer:

A chloride free Sulphonated Naphthaline Polymer (CONPLAST SP430) was used in this study. It is deep brown in colour and is capable of dispersing instantly in water. It complies with the specifications of IS 9103:1979 and IS 2645:1975. Some characteristics of CONPLAST SP430 are given in Table 4.5.

4.2.6 Water:

Potable tap water being supplied at CBRI, Roorkee was used for mixing of concrete and curing of test specimens. The water used, contained no impurities like chloride.

4.3 Proportioning and mixing of concrete:

The ACI Method of mix design was used for calculating the proportions of concrete used in present study. To be able to maintain a uniform workability of the fresh concrete to the extent possible, the total water content and the coarse aggregate content in all the mixes were kept constant. It was further considered desirable to maintain the volume fraction of the aggregate so that the effect of this parameter on the chloride diffusion could be marginalized. Table 4.6 shows the mixture proportions of the twelve mixes, which were used to prepare the test specimens. Various ingredients of the concrete mix are dealt below.

4.3.1 Water binder ratio:

All discussion in this thesis has been reported in terms of the binder content which is the sum of the cement (OPC) and the slag used. To study the effect of water-binder ratio,

three different W/B ratios of 0.4, 0.5, and 0.6 were used for all replacement levels as well as the control concrete. Though a high water binder ratio of 0.6 is not desirable for concretes exposed to chloride environment (and use of such high W/B ratio is also not permitted by codes of practice), yet it has been included in the present study to accelerate the penetration of chlorides.

4.3.2 GGBS proportions:

Three replacement levels of OPC with GGBS were adopted: 35, 55, and 75% by weight of total binder content.

4.3.3 Water content:

As mentioned earlier, to keep the workability of the all the fresh mixes uniform, the total water content was kept constant at 180 Kg/m³ in all the mixes.

4.3.4 Coarse aggregate:

The coarse aggregates, which were present in two size ranges as mentioned earlier, were mixed in ratio 1:1. The total coarse aggregate content in all the mixes was also kept constant at 1098 Kg/m³, so that effect of this parameter on the resistance to chloride penetration remains same for all mixes.

4.3.5 Fine aggregate:

Since the coarse aggregate content was kept constant, the fine aggregate was also nearly constant for a particular W/B ratio except for small changes due to replacement of OPC by GGBS, which has slightly lower specific gravity.

4.3.6 Superplasticizer:

To improve the workability and to incorporate the recent trends of mix proportioning, superplasticizer was also added to the mixture while mixing. The dose of superplasticizer was taken as 1% by weight of total cementitious material.

4.3.7 Mixing the concrete:

The concrete ingredients were mixed in the laboratory in a drum mixer. The surface and blades of the mixer were moistened before mixing began to avoid absorption of mixing water onto mixer surfaces. This was carried out for all mixtures so as to ensure a uniform mixing condition. The mixing procedure is explained step by step below.

- (i) The coarse and fine aggregates were first put in the mixer and mixed properly.
- (ii) Cement and slag, which was hand mixed properly to get a uniform colour, were added to the mixer and the ingredients mixed in dry condition for about 2 minutes so as to attain a uniform colour of the mix.
- (iii) About 80% of the mixing water was added to the mix and mixing was continued for 2 minutes.
- (iv) The required dose of superplasticizer was added to the remaining part of the mixing water, where it dispersed quickly, and it was added to the mix.
- (v) After 2 to 3 minutes, when it was seen that the mixing is uniform and proper, the mixed concrete was discharged from the mixer on a clean iron sheet.
- (vi) Just after the concrete was discharged from the mixer, a part of it was taken for measuring the compaction factor. The compaction factor of the fresh concrete of all the mixes was in the range of 0.845 ± 0.015 .

4.4 Casting and curing of specimen:

Cast iron moulds and table vibrator were used for casting of cubes. All moulds were lubricated by applying a very thin layer of oil on the inner surface of the moulds and placed on the vibration table. Fresh concrete was filled in the moulds in two layers, with each layer being adequately vibrated. It was noted that vibration of each layer took approximately 1 to 1.5 minute.

The cube specimens were then removed from the vibration table with the moulds and stored in the laboratory. They were covered with wet jute bags after about 6 hours of casting. The specimens containing 0 and 35% GGBS were demoulded 24 hours after casting whereas those containing 55 and 75% GGBS were demoulded 48 hours after casting. All the concrete cubes were submerged in a large tub containing tap water for bath curing, immediately after demoulding.

It was unfortunately not possible to regulate the temperature of the curing water. It is important to note that the casting was carried out in October, 2000 and the specimens were used till about end of April, 2001. The region (Roorkee) where the work was carried out experiences winter season during most of the mentioned period and the temperature ranges between 5 to 25°C. The temperature goes below 5°C during nights in the months of December and January.

4.5 Experimental procedure:

The specimens used in the present study were concrete cubes of 100mm side length, except for 3 specimens of each mix that were of 150mm side length. Three cubes of 150mm edge length were cast to compare the compressive strength of these cubes at 28 days to that

of cubes with 100mm edge length, cast with same mix. However, all other tests were performed on 100mm size cubes of twelve mix types discussed earlier.

4.5.1 Compressive strength test:

The compressive strength tests were carried out at the ages of 1, 4, 8, 12, and 24 weeks after bath curing in water tub. Three test cubes of 100mm size were used for each of the compressive strength tests and the average value of the three has been reported. In addition three additional cubes of size 150mm were used to measure the compressive strength of each mix at a bath-cured age of 28 days, as prescribed by the IS: 516-1959. For testing of the compressive strength of any mix, three cubes of that mix were taken out from the tub and were left for some time so as to become surface dry but still remain saturated. Then the cubes were tested the procedures described in IS: 516-1959. The tests were carried out at the structural engineering laboratory of CBRI, Roorkee.

4.5.2 Chloride penetration studies:

As mentioned earlier chloride penetration studies were conducted on 100mm cube specimens for all the 12 mixes. All the specimens were first bath-cured in pure tap water for 28 days before being submerged in chloride solutions. After 28 days of curing 6 cubes of each mix were taken out from the water tub and left to dry partially for 5 hours. Then 3 cubes of each mix were submerged in sodium chloride (NaCl) solutions of concentrations 3.5% and 7.0% by weight, prepared by mixing NaCl to potable tap water in the laboratory. The cubes were placed in the containers containing the solutions with their bottom face (while casting) downward. These cubes were kept submerged continuously in the NaCl solution till the time of sampling for chloride penetration analysis. In addition 6 cubes each of all the mixes having w/b ratio of 0.6 were taken out from curing tub and put in the NaCl

solutions, three in each, for studying chloride penetration in wetting and drying conditions. These cubes were alternately submerged and taken out from the solution after fix durations. 8 hours was taken for drying cycle and remaining 16 hours of day was taken for wetting cycles. The drying was done at the room temperature and relative humidity by just placing the cubes out side the containers in the laboratory.

4.5.2.1 Simplifications in exposure procedure:

Based on the literature survey and past experiences some simplifications were done in the present study in the exposure procedure and analysis of chloride from that usually followed in concentrated immersion tests. Usually out of six faces of the specimen, five faces are coated with waterproof materials/paints, and ingress of chloride is allowed through one face only, so as to simulate it to the theoretical model of one dimensional diffusion in semi- infinite media. But, we all know from past observations that chloride ion penetration in matured concrete is not that fast and ions usually are unable to penetrate in the cube beyond 25mm from surface, in a six months duration, which was the observation period in this experiment. Thus, if we collect the concrete powder for analysis by drilling vertically at the center of any face of the cube, the influence of the other faces can be ruled out.

Secondly, while casting the cubes, special attention was given on the fact that all the cubes of a particular mix are uniformly casted and compacted. Thus, it was assumed that all the cubes with same mix content and similar exposure conditions would show similar diffusion properties. Therefore, while sampling the powder for analysis at a particular age of submersion in NaCl solution, only one cube was taken out from each solution and sampling was done from its four similarly exposed side faces, leaving the top and bottom one. The concrete powder collected from these faces were mixed properly before analysis. After

collection of the powder no sealing of the holes of cubes was done for further studies and the cubes were discarded altogether for further use. For analysis at further exposure durations another cube of same mix was taken out.

4.5.2.2 Sampling of concrete powder:

One cube of each mix was taken out from the NaCl solution after the intended exposure period was over, i.e. after 6, 12, and 24 weeks of exposure. Also one cube was taken out from each mix exposed to wetting and drying exposure conditions at same exposure ages. After taking out, the surfaces of the cubes were quickly and slightly washed by tap water. Then they were left for drying for three days. After the cubes become completely dry, at least near the surface, drilling was started using a 25.4mm Φ drill. The tip of the drill was slightly tapered as shown in figure 4.1.

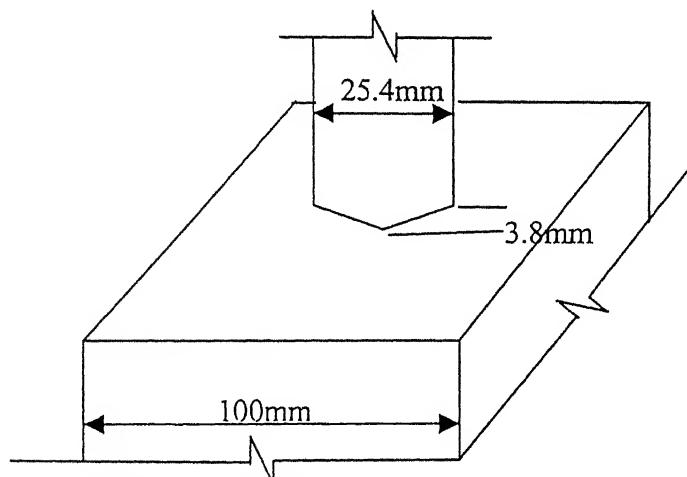


Figure.4.1 Drill-Bit and Cube Specimen

The measurements for depth of drilling were taken with reference as tip of the drill being just placed at the cube surface gives zero reading. The drilling was done vertically at the center of the four side faces of the cubes. In the first step drilling was done upto a depth

of 3mm and the powder thus obtained was discarded. Further drilling was carried out in steps of 5mm depending upon the factors such as W/B of the mix, GGBS replacement level, age of exposure etc. While drilling the gaze was fixed in the drill for a particular depth and all the cubes were first drilled upto that depth. The powder collected from the four faces of a single cube was mixed properly and was placed in small plastic bags.

4.5.2.3 Preparation of solution:

Following steps were performed for preparation of solution for chloride analysis of the sampled concrete powder.

- (i) The concrete collected from different drill holes of a particular cube specimen were thoroughly blended by transferring the material from one glazed paper to another at least 10 times.
- (ii) The powder was weighed using an analytical electronic balance, upto milligram precision. Approximately 4 to 5 gm of powder was taken from powders thought to be containing higher chloride concentrations i.e., from the powders collected from lower depths, and about 8 gm powder was taken from samples thought to be containing lower chloride concentrations i.e., from the powders collected from comparatively greater depths.
- (iii) The weighed powders were carefully collected in small paper envelopes, taking care that no loss of fine particles takes place.
- (iv) For determination of acid soluble chlorides, the weighed powders were placed into 250ml capacity borosil beakers. Then 10ml of 1:1 dilute nitric acid (HNO_3) was added to them and the solution was stirred properly with mixing rods.

- (v) 40ml of distilled water was added to the solution obtained in step (iii) and the solution was again stirred properly.
- (vi) This solution containing 50ml liquids was weighed on a physical electronic balance with 0.01gm least count.
- (vii) The solution was heated slowly to boiling and was boiled for about 1 to 2 minutes.
- (viii) The boiled solution was allowed to cool to room temperature and again weighed on the physical electronic balance.
- (ix) The loss of weight due to boiling was compensated by adding appropriate amount of distilled water to the cooled solution.
- (x) All the above steps other than step (iii) were also followed for determining water soluble chlorides, only instead of adding 40ml distilled water as mentioned in step (v), 50ml of distilled water was added.
- (xi) The solution was allowed to stand still without any disturbance for about 1.5 hours so that the particles of concrete settle down in the beaker leaving a clear solution on the top.
- (xii) Sufficient clear solution was decanted from the settled solution in another 250ml beaker.

4.5.2.4 Analysis of the prepared solutions:

For determining the chloride contents of the sampled powders potentiometric titrations were performed on 10ml decanted clear solutions prepared from them. The solutions were titrated against 0.01N AgNO_3 solution, using a high precision auto titrator.

The electrode used for the titrations in present study was ionic selective Combined Massive Ag Electrode.

The percentage of chloride in the concrete powder was finally calculated using the formula:

$$\text{Percentage of chloride in concrete powder} = [(K * N * V) / W] \%$$

Where,

K = A constant, depending upon total volume of solution made

And the volume of solution take for titration,

Here, $K=17.75$

N = Normality of AgNO_3 solution, here equal to 0.01

V = Volume of AgNO_3 dispensed to reach the end point

And, W = Weight of the concrete powder.

The details of the titration process, the reagents and chemical used, and the precautions taken are given in the Appendix [2].

NOTES:

1. The reference laboratory methods for determining chlorides in cement or concrete usually prescribe filtration of the solution to separate solid residues from it. But here the filtration step has been eliminated for simplifying laboratory procedure, speeding up the titration of the lot many samples, and reducing the risk of yielding erroneous results due to incomplete filtration. Though, some apprehensions may be made about the presence of solid

residues affecting the ionic activity in solution, but the step is justified here because

- Sufficient time was given for settling of the solid residues.
- Only the clear portion was decanted slowly.
- Some previous works on potentiometric titration without filtration step i.e., containing all the concrete powder in the solution for titration [Climent et al, 1999], report that potentiometric titration based on Grand's method of end-point detection allows the elimination of filtration step or even decanting, without affecting the accuracy and reliability of the analysis.

2. The titration performs better in acidic media. It was observed in case of titrations of solutions containing water-soluble chloride, especially in case of low chloride concentrations, that some fluctuations were there in recording the potential and sufficient time was taken to reach equilibrium, if the solution was not made acidic.
3. Presence of sulphates affected the determination of chloride concentrations especially in low concentration water-soluble chloride solutions. It was observed from development of some blackish precipitate of Ag_2S apart from the usual white precipitate of AgCl . And due to this reason in some cases the consumption of AgNO_3 was more so as to give water-soluble chloride concentration even slightly greater than acid-soluble chloride concentration.

To counter it Hydrogen Peroxide (H_2O_2) was added to the solution for analysis in such cases, so that the sulphates are oxidized.

4. Though heating was done for all the samples, as prescribed in reference methods, it was just tried and observed for some samples that it does not make any significant difference.
5. From the available literature and reports it can be observed that there is still an ongoing controversy about the convenience of determination of the acid-soluble or the water-soluble chlorides in concrete.

**Table 4.1: Chemical composition and physical properties of cement
(Birla Uttam OPC, Grade C43)**

<i>Chemical composition</i>	<i>% by wt. of cement</i>
SiO ₂	21.41
Al ₂ O ₃	8.95
CaO	62.25
Fe ₂ O ₃	2.80
MgO	1.46
SO ₃	2.65
<i>Physical properties</i>	
Specific gravity	3.14
Blaine's fineness	2546 cm ² /gm
Standard consistency	0.30
Initial setting time	75 min.
Final setting time	295 min.
Loss on ignition	0.30%

Table 4.2: Chemical composition and physical properties of GGBS

<i>Chemical composition</i>	<i>% by wt. of GGBS</i>
SiO ₂	33.2
Al ₂ O ₃	18.3
CaO	32.9
Fe ₂ O ₃	0.6
MgO	11.6
SO ₃	1.0
S	0.7
K ₂ O	0.91
Na ₂ O	0.21
Li ₂ O	0.5
MnO	0.43
Cl	0.006
<i>Physical properties</i>	
Specific gravity	2.91
Blaine's fineness	3300 cm ² /gm
Glass content	93%
Bulk density	1.1
Colour	Dull white

Table 4.3: Properties of coarse aggregate

<i>Physical properties</i>		
	20mm size	10mm size
Specific gravity	2.673	2.687
Bulk density	1.609gm/cm ³	1.575gm/cm ³
Water absorption	0.47%	0.24%
<i>Sieve analysis / grading</i>		
<i>IS Sieve</i>	<i>Percentage by weight passing</i>	
20mm	99.5	100.0
16.4mm	85.8	100.0
12.4mm	22.2	89.4
10mm	3.6	29.6
4.75mm	0.2	0.05
2.36mm	0.0	0.0

Note: Combined bulk density of the two aggregates, when mixed in ratio 1:1 is 1.613 gm/cm³.

Table 4.4: Properties of fine aggregate

<i>Physical properties</i>		
Specific gravity	2.55	
Bulk density	1.496	
Water absorption	0.7%	
Fineness modulus	2.52	
Colour	Reddish	
<i>Sieve analysis</i>		
IS sieve	Cumulative % retained	% Passing
4.75mm	0.67	99.33
2.36mm	1.81	98.19
1.18mm	11.34	88.66
600 μ m	50.27	49.73
300 μ m	89.26	10.74
150 μ m	98.32	1.68

Table 4.5: Characteristics of superplasticizer

Specific gravity	1.11 at 30°C
Chloride content	Nil
Air entrainment	1% approx.
Compatibility	Can be used with all types of cements and admixtures when added separately with mix.

Table 4.6: Mixture proportions in per cubic meter of concrete

Mix Designation	W/(C+S) Ratio	% of Slag	Water Content (Kg)	Cement (Kg)	GGBS (Kg)	F.A. (Kg)	C.A. (Kg)	SP (l)	Measured C.F.
A1	0.4	0	180	450.0	0.0	659	1098	4 1	.847
B1		35	Do	292.5	157.5	648	Do		.955
C1		55	Do	202.5	247.5	641	Do		.852
D1		75	Do	112.5	337.5	634	Do		.860
A2	0.5	0	Do	360.0	0.0	722	Do	3.3	.854
B2		35	Do	234.0	126.0	713	Do		.843
C2		55	Do	162.0	198.0	708	Do		.840
D2		75	Do	90.0	270.0	703	Do		.858
A3	0.6	0	Do	300.0	0.0	773	Do	2.7	.831
B3		35	Do	195.0	105.0	762	Do		.842
C3		55	Do	135.0	165.0	756	Do		.838
D3		75	Do	75.0	225.0	751	Do		.836

Note: The symbols given in the table are as follows, W (water), C (cement), S (GGBS) F.A. (fine aggregate), C.A. (coarse aggregate), SP (superplasticizer), and C.F. (compaction factor)

Chapter 5

RESULTS AND DISCUSSION

5.1 Introduction

As has been stated earlier in this thesis, compressive strength and chloride penetration in concretes containing GGBS were used as parameters for evaluating the performance of such concretes. This chapter presents the results obtained and discussion on them.

5.2 Results of compressive strength tests

The compressive strength of 100mm cubes of all the mixes at different ages is given in the Table 5.1. This table also gives the compressive strength of 150mm cubes at 28 days. It can be seen from the results that the compressive strength given by 150mm is 12-14% higher than that given by 100mm cubes.

5.3 Results of chloride penetration studies

The results of chloride penetration analysis are given in Tables 5.2, 5.3 and 5.4. Table 5.3 and 5.4 give the total chloride concentration at different depths for samples that were continuously immersed in 3.5% and 7.0% NaCl solutions respectively. Table 5.4 gives the values of total chloride penetration in case where alternate wetting and drying of samples with chloride solution was applied.

As stated earlier also, it is sometimes argued that rather than the total chloride, it is the water-soluble chloride that is harmful the point of view of reinforcement corrosion. Further doubts have been raised about the chloride binding capacity of concretes containing

slags (in view of the total C₃A content in the system). Therefore, water-soluble chlorides were also determined for some of the samples. The results obtained are given in Tables 5.5, 5.6 and 5.7

5.4 Discussion on compressive strength

5.4.1 Results from 100mm and 150mm cubes

As can be seen from the results given in Table 5.1 the compressive strength obtained from 150mm cubes is found to be approximately 12 to 14 % greater than that found from 100mm cubes in all cases. It is well known that mechanical properties of quasi-brittle materials like concrete show dependence on the size of the specimen [Carpinteri et al, 1999]. In literature, two size effect laws have been used to model the scale effect on the compressive strength of concrete, multifractal scaling law (MFSL) and size effect law (SEL). Theoretically speaking the ultimate strength should decrease with increasing size of concrete structure of a given geometry. But in this study it has been found to be contrary. Though more data is required to clearly establish the reason for the results obtained here, the greater strength obtained here in the 150mm cubes can be attributed to better compaction of concrete in larger cube moulds.

5.4.2 Strength development in concretes containing GGBS

From the Table 5.1 it can be easily interpreted that though the compressive strength of GGBS incorporating concretes is less at early age of 7 days, the percentage increase in strength at further ages in these concretes is higher than that in OPC concrete. For a given proportion of GGBS the percentage increase in the strength, as compared to that of OPC concrete, increases with increasing water to cementitious material ratio, the same has also been reported by Meusel and Rose, 1983. Also a higher continued strength

gain till 168 days is observed in GGBS containing concretes.

5.4.2.1 Strength at 7 days:

To have a clearer picture the results have also been compared graphically. Figures 5.1, 5.2 and 5.3 compare the results of compressive strength of concretes containing different GGBS replacements to corresponding OPC concrete of w/b ratio 0.4, 0.5 and 0.6 respectively. It is seen that at an age of 7 days the strength of all the GGBS concretes is lower than that of OPC concrete of respective w/b ratio. The data given in Table 5.1 is represented differently in Table 5.8, which gives the compressive strength of all the mixes as the percentage of 28 days compressive strength. From this table it is clear that at 7 days the highest percentage of 28 days strength is obtained by OPC concretes (no slag content) for all w/b ratios and the percentage strength obtained by GGBS concretes goes on decreasing as the replacement level increases. In terms of strength obtained at 84 days or 168 days, the percentage of strength obtained by GGBS concretes at 7 days will be further lower because GGBS concretes gain more strength than OPC concretes after 28 days. Figure 5.4 shows the variation in 7 days compressive strength with increase in GGBS content for all the water binder ratios.

5.4.2.2. Strength at 28 days:

Design codes often refer to the 28 days strength of concrete and quality control is usually carried out on the basis of strength at this stage. Special attention therefore needs to be paid to strength at 28 days. The results presented in Table 5.1 clearly show that the strength of GGBS incorporating concrete is lower at 28 days also, but the difference narrows significantly from that at 7 days. The strength of 35% GGBS concrete almost equals the compressive strength of control concrete, whereas that of 55% GGBS concrete

approaches it. The variation in compressive strength at 28 days with the increase in GGBS replacement level is shown in Figure 5.5.

5.4.2.3 Long-term strength:

It has been often argued that concrete containing slag (or other pozzolana) continues to gain strength over a much longer period of time, as a result of reaction between CH and slag. Tests of compressive strength were therefore continued to obtain data for 56, 84 and 168 days also.

It can be seen from the Table 5.1 that at 56 days the strength of 35% GGBS concrete becomes higher than that of control concrete, while the 55% replacement concrete just approaches the compressive strength of control concrete. Ultimately we see that at the age of 168 days 55% concrete also just crosses the strength of plain concrete though marginally. The 75% replacement level gives lower strength at all ages and the highest strength in the observation period has been given by 35% replacement of OPC by GGBS in all cases. The strength development in GGBS concretes is delayed because the hydration of GGBS is effected by pozzolanic reactions of GGBS with $\text{Ca}(\text{OH})_2$ which is available after hydration of cement only.

It is also clear from Table 5.8 that the percentage gains in compressive strength after 28 days, which is more for GGBS concrete, is more for higher replacement levels at higher w/b ratios. For example, at w/b ratio of 0.4, the 35% replacement level concrete gains 38% from its 28 days strength, which remains more or less constant for other w/b ratios of 0.5 and 0.6 also. Whereas, at 75% replacement level the gain in compressive strength from that of 28 days goes on increasing with increase in w/b ratio and maximum percentage gain (65%) is given at the water binder ratio of 0.6. The picture becomes clearer from the Figure

(5.9) giving plot of percentage increase in strength from 28 days strength and w/b ratios for all replacement levels. It can be seen from this figure that the gain in strength for 35% GGBS concrete is consistent (near 40%) at 168 days for all w/b ratios, whereas that for 55% replacement level higher gain is shown at w/b of 0.5 than that at 0.4 and the gain at w/b of 0.6 is again nearly same as that at 0.5. For GGBS replacement level of 75% we see that the percentage gain in strength after 28 days consistently increases from that at 0.4 to that at 0.6. So, we see that larger the w/b ratio, i.e. larger the porosity, larger is the scope for GGBS to show its potential. As stated earlier Meusel and Rose, 1983, have also reported similar findings.

The trend in strength development found here is similar to that reported earlier i.e., initially the strength of GGBS concrete is less but continued strength development takes place in them for longer period, and ultimate strength obtained is either equal or higher than the OPC concrete up to 55 to 60% replacement levels. Generally 50% GGBS is taken as optimum proportion from strength point of view. In this study also, as is evident from Figures 5.6, 5.7 and 5.8 showing strength for different replacement levels at 56, 84 and 168 days respectively, it can be seen that the maximum strength is given by the replacement level somewhere between 35% and 55%. Here also it can be seen that the potential of higher replacement level is best extracted at higher w/b ratios. It can be seen from Figure 5.8 that 35% replacement level gives maximum strength at 168 days at 0.4 w/b ratio, while at 0.6 w/b ratio maximum strength is given by 55% GGBS concrete. The decrease in compressive strength after a replacement level of 50-55 % can be explained on the basis that in that case sufficient $\text{Ca}(\text{OH})_2$ may not be present to complete the pozzolanic reactions.

5.4.2.4 Concluding remarks:

Based on above discussion it can be suggested that in the case of use of GGBS in concrete 91 days strength is more representative of its ultimate compressive strength. This can be incorporated in specifications, with a specific guideline for delayed removal of formwork to take care of slow initial strength development.

5.5 Discussion on chloride penetration

5.5.1 Discussion on the basis of chloride concentrations at different depths

Graphs of chloride concentration versus drilling depth have been drawn for all the observed values given in Tables 5.3, 5.4, and 5.6. The chloride penetration profiles for different cases are plotted in Figures (5.10-5.33), to compare the resistance to chloride penetration of concretes with different GGBS replacement levels. From studies of chloride penetration at 6 and 12 weeks it was observed that very low penetration took place up to 20 mm so further drilling was not done, but at the exposure age of 24 weeks drilling was done up to 25 mm.

Though these results are discussed in greater detail in this section, it is clear from the results given in above-mentioned tables and figures that GGBS incorporation in concrete significantly reduces chloride penetration. It can also be mentioned here, that though the results are inconclusive at lower ages of experiment but at higher age of 24 weeks the reduction in chloride penetration is dramatically increased.

5.5.1.1 Effect of slag replacement level:

It is observed from the results and their analysis that the improvement in resistance to chloride penetration increases with increase in the replacement level of OPC by GGBS,

and the minimum chloride concentrations as well as penetration depths are given by 75% GGBS concretes in the present study. The effect of replacement level on the chloride penetration is seen to be most dominant of the various parameters considered in this study. It can be seen from Figures 5.30 and 5.31 that for concrete containing 55% and 75% GGBS, virtually there is no penetration at 20 mm and 25 mm depths even at exposure age of 24 weeks and high water binder ratio of 0.6. Whereas the control OPC concrete, with no GGBS, shows significant chloride penetration at these depths in similar exposure conditions. This reduction in chloride penetration can be attributed to the pore refinement of concrete containing GGBS due to the hydration of slag.

5.5.1.2 Effect of w/b ratio:

As is expected the chloride penetration in concrete increases with increase in w/b ratio. But the effect of w/b is more dominant in OPC concretes, where as high replacement level concrete perform better at higher w/b ratio also. For a given replacement level (for higher replacement values) the percentage improvement in chloride penetration resistivity increases with the increase in the w/b ratio. It can be attributed to the larger pore volume in the higher w/b ratio concretes, which can be filled and densified through the continued reaction of slag with the calcium hydroxide and alkalis released during the Portland cement hydration.

5.5.1.3 Effect of cyclic wetting and drying:

It has been observed that the problem of reinforcement corrosion is most severe in those zones of marine and other structures that are exposed to cyclic exposure to chlorides. The results shown in Table 5.5 for cyclic exposure have been compared with those obtained under constant immersion and plotted in Figures 5.34, 5.35, and 5.36.

It can be seen from these figures that there is not much difference in chloride penetrations in cyclic wetting and drawing case and continuous immersion case. It can be seen in these figures that the best-fit line almost coincides with the line of equality. It can be explained on the basis that though the penetration due to simultaneous action of capillary absorption and diffusion is expected to be faster but the total time for which the specimen is actually immersed in chloride solution in cyclic exposure is much less. Hence the increase in chloride concentrations in cyclic exposure is not very significant. Tang and Sandberg, 1996, also reported similar findings from their a year long study.

5.5.1.4 Soluble vs. total chloride:

From the observed values of soluble chlorides and their ratio to the total chloride presented in Tables 5.6-5.8 no clear effect of incorporation of slag on chloride binding is shown. Also the soluble chloride values observed here may be slightly higher due to influence of sulfides present in the concrete. While determining the water-soluble chloride it was observed that the presence of sulphur noticeably affect the results, especially in case of lower chloride concentrations. In some cases development of slightly black colour due to formation of Ag_2S was clearly visible. The results showing clearly the presence of significant amount of slag has been discarded and are not reported here.

It should be noted that the determination of soluble chloride at some particular time in the life of a cement system might be substantially different than that at other time. For example the percentage of free chlorides, calculated with respect to corresponding total chlorides, observed at 6 weeks exposure age is higher than that observed at 24 weeks exposure age. From Table 5.6, it can be seen that at 6 weeks age (immersion in 3.5% solution) the values of free chlorides ranges between 81-95 % with an average of 87%.

Whereas, free chlorides observed at 24 weeks, given in Tables 5.6 (immersion in 3.5% solution) and 5.7 (immersion in 7.0% solution), ranges between 50-89 % with an average of 77% and 58-87 % with an average of 78% respectively. The values of soluble chlorides are also plotted against total chloride in Figures 5.37, 5.38, 5.39 and 5.40 and best-fit linear line has been drawn. Here also same thing can be observed with ease.

The free chloride concentrations observed here are higher also because the cubes were exposed to salt solution only after maturity when most of the hydration reactions were complete. It will also be appropriate to mention here that the water-soluble chloride determination may be significantly affected by test conditions. Therefore, care should be taken when comparing results from one test method with those from other test methods, as is also suggested by ASTM C1218, giving the test methods for determination of water-soluble chloride.

5.5.2 Estimated apparent diffusion coefficient (D) and pseudo equilibrium surface concentration (C_S)

Diffusion coefficients and the surface concentration for all the mixes and all the three ages of experimentation were also determined assuming the validity of Fick's laws of diffusion for one dimensional diffusion case. The diffusion coefficient and surface concentration values were found by fitting the observed values on the equation (5.1) and finding the constants giving the least mean square error.

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad \dots \quad (5.1)$$

Where, $\operatorname{erf}(z)$ is the standard error function, given as:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$

The values of apparent diffusion coefficients and pseudo equilibrium surface concentration have been given in Tables 5.9, 5.10 and 5.11 for submersion in 3.5% and 7.5% NaCl solutions and for alternate wetting and drying exposures respectively. Table 5.12 presents the diffusion coefficient values for different mixes and different exposure conditions and following paragraphs present the results briefly.

5.5.2.1 Effect of GGBS replacement level:

As can be seen from the results given in Table 5.12 that the diffusion coefficient of concrete reduces significantly due to incorporation of GGBS at all ages and especially at higher ages. It should also be noted from the Tables 5.8, 5.9 and 5.10 that the values of pseudo equilibrium surface concentrations of chloride ions in higher GGBS concretes are also slightly lower than that in OPC concretes in most of the cases.

5.5.2.2 Effect of w/b ratio:

As is expected the diffusion coefficient increases as the w/b ratio of concrete increases. But for higher replacement levels of GGBS the effect of w/b ratio is much less than that in OPC concretes, especially at higher ages. At 24 weeks exposure duration the 75% GGBS replacement concrete performs equivalently at all w/b ratios. It can be also seen from the Table 5.12 that of the two, w/b ratio and replacement level effect of higher replacement level is dominant on the diffusion coefficient.

5.5.2.3 Effect of exposure concentration:

The calculated values of diffusion coefficients and surface concentrations for 3.5% immersion solution are plotted against that for 7.0% immersion solution, and presented in Figures 5.41 and 5.42 respectively. It is interesting to note from the results that though

there is significant increase in the observed chloride concentration at different depths due to increase in the concentration of exposure solution, there is only slight increase in diffusion coefficient. The increase in penetration inspite of comparable diffusion coefficient is due to increase in pseudo equilibrium surface concentration (C_s), plotted in Figure 5.42, due to higher concentration of solution. If we go by the average, i.e. the best-fit line, it can be observed from the figure that the ' C_s ' values almost doubles due to increase in exposure concentration from 3.5% to 7.0%.

Thus, it can be seen that in immersion test the chloride ion concentration does not affect the transport properties of concrete, whereas in migration tests under applied electric field the external chloride concentration plays significant role in determination of transport properties as reported by Andrade et al, 1996. Andrade et al observe that though higher external chloride concentrations are proposed for accelerating the chloride penetration in migration tests, D values decrease with increase in chloride concentration due to the higher ion-ion interaction, due to increased ion concentration. But as we observe from present study, in concentrated immersion test higher immersion concentrations can be advantageously used to accelerate the test without affecting D values significantly. And it is so that the Danish Standard APM-302 suggests an immersion concentration of 3-5 M, i.e. 18-30% by weight.

5.5.2.4 Effect of cyclic exposure:

The effect of cyclic exposure on the penetration of chloride has been analyzed by plotting the ' D_{app} ' values for continuous immersion against that for cyclic wetting and drying at different ages. The plots are given in Figures 5.43, 5.44 and 5.45 for exposure durations of 6, 12, and 24 weeks respectively. It is very clear and interesting to note from

the best- lines as well as the scattered point in these figures that though the diffusion coefficient values increases in cyclic exposure, the effect diminishes with passes of time. It can be observed that the values of diffusion coefficient in cyclic exposure ' D_{wd} ' are much higher at 6 weeks immersion age than the diffusion coefficient values in continuous immersion ' D_{imm} '. The ' D_{wd} ' values are also higher at 12 weeks immersion age, but the difference decreases sharply. And finally at 24 weeks immersion duration the values of both ' D_{wd} ' and ' D_{imm} ' comparable.

The above observations can be explained on the basis that at lower ages the chloride concentration profiles are more dominated by the values near the surface, where the capillary absorption is more effective. But at higher exposure durations, concentration of chlorides at greater depths also increases and they also significantly influence the concentration profile, therefore diffusion plays the dominant role.

5.5.2.5 Variation of D with age:

The change in diffusion coefficient with time can be easily interpreted from the Table 5.12 and the Figures (5.46-5.53) showing plot of diffusion coefficient verses time of exposure. It can be seen from these figures that though the diffusion coefficients of concrete containing GGBS is not much less at early exposure duration (6 weeks), it decreases dramatically with time and at the exposure age of 24 weeks there is manifold decrease in the diffusion coefficient of concretes containing GGBS. Again it can be seen that the effect is magnified with increase in w/b ratio. As can be seen from the Table 5.12, at the age of 24 weeks 'D' of 55% and 75% replacement concretes are only 50%, 33% and, 25% of the 'D' of OPC control concrete for W/B 0.4, 0.5 and, 0.6 respectively.

Also, after 24 weeks, any decrease in diffusion coefficients is not expected for the plain cement concretes, whereas a high decrease in the diffusion coefficient values of GGBS concretes, especially for replacement levels of 55% and 75%, is still expected.

5.6 Chloride diffusion vis-à-vis compressive strength

Civil engineers often believe that ensuring adequate strength is enough to ensure durability as can be borne out by specifications on the maximum W/B under severe conditions of exposure, etc. However, results from the present study show that with incorporation of GGBS in concrete the improvement in impermeability is always obtained inspite of the fact that the strength of the GGBS containing concretes decreases or at the most is comparable if we go for replacement levels higher than 50%.

It can be explained on the basis that the strength depends upon the total porosity of the concrete matrix whereas the chloride permeability depends not only upon the total porosity but also upon the fineness of the pores and their distribution in the concrete and the conductivity of the chloride pore solution. D.M Roy, 1986, reports that with increased fly ash replacement (40%) ratio, the permeability to water and, especially, to chloride ions is dramatically decreased although the porosity is increased.

Several investigations have shown, using mercury insertion techniques, that incorporation of GGBS in cement paste helps in the transformation of large pores in the paste into smaller pores, resulting in decreased permeability of the matrix. In a study reported by D. M. Roy, 1989, upon cement pastes and mortars incorporating separately ground slag, it was observed that pores with radius finer than 5 nm dominated the pore structure of hardened slag-containing pastes, whereas in OPC pastes the majority pores range from 5-20 nm.

Also it should be noted that water permeability is quite different from chloride permeability. Diffusion of chloride ion is an ionic diffusion and is influenced by its interaction with the cations present in pore solution. So, besides the physical improvement in pore structure changes in chemical composition may also cause the reduction in chloride transport rate upon incorporation of GGBS.

So, if ordinary Portland cement is used then the strength of the mix can be taken as a parameter for ascertaining the durability of structures exposed to chloride salts, but the same is not true when using supplementary cementitious materials (SCM) like GGBS. And in that case permeability of the concrete matrix should be taken as a completely independent parameter. It can be observed from the above results that the effect of proportions of GGBS is much more on the chloride permeability of concrete than on the strength, and improvement in impermeability is always obtained even if the strength is adversely affected.

5.7 Diffusion Coefficient and service life

Estimation of diffusion coefficient (D) from the observed chloride penetration profiles is important not only because it gives a quantitative measure of diffusivity of the concrete matrix, but also because it is an important parameter for estimating the chloride concentration at certain depth at any point of time in future. Accordingly concrete cover over the reinforcement can be specified in aggressive environments, and if sufficient and realistic data are available, the diffusion coefficient can also be taken as a design parameter for design of the mix proportions as well as the structure.

The above results show that the diffusion coefficient is not constant with respect to time and there is significant decrease in it with time especially in case of high GGBS

concretes. The decrease in 'D' with time depends upon the GGBS replacement level and the w/b ratio, and there is some consistent trend in its decrease. These results suggest that if sufficient data (long term), collected for different replacement levels and for different w/b ratios is available, it may be possible to develop a relation giving variation of 'D' with time and also including replacement ratios and w/b ratios, as one is given by Thomas et al, but for 70% replacement and a particular w/b ratio only. And if 'D' is a function of time, Fick's second law is still valid, and its solution can be obtained by slightly modifying the equation by introducing a new function as described in Chapter 3 of the thesis. Thus the critical time required to reach the threshold chloride level near the reinforcement can be accurately calculated, which otherwise is very conservatively estimated based on the diffusion coefficients at early ages.

From the above mentioned standard solution of the Fick's second law, for a semi-infinite media, it is clear that if other parameters like threshold chloride level required for activation of protecting film, the concrete cover (x) and ' C_s ' are taken same then time 't' for initiation of corrosion is inversely proportional to the diffusion coefficient. Though we observe here that there is an increase in C_s values with time, but it is reasonable to think that it attains saturation and becomes constant with passes of time. Takewaka et al also report from field as well as laboratory studies that the chloride concentration in concrete is nearly constant at surface and ranges between 0.7 to 1.0% by weight of concrete. So, we can have as many fold increase in the service life as there is decrease in the diffusion coefficient. And if we keep the service life as constant then the cover required is directly proportional to the square root of diffusion coefficient. Therefore, we can see that with

incorporation of GGBS thickness of cover to reinforcement can be safely reduced to half or even less for same service life of structure [Takewaka et al]

Table 5.1: Compressive strength of the concrete mixes at different ages.

Mix	Compressive strength (N/mm ²)				
	7 days	28 days **	56 days	84 days	168 days
A1	29.5	35.3 (41.0)	36.8	37.5	42.0
B1	26.5	34.2 (37.5)	42.0	42.5	47.2
C1	23.0	31.8 (35.8)	36.8	37.5	39.2
D1	20.3	29.0 (32.6)	33.3	34.2	36.8
A2	23.7	30.4 (34.6)	33.5	34.8	36.5
B2	22.1	30.2 (34.6)	36.5	38.5	40.8
C2	17.5	27.6 (31.4)	30.4	31.8	39.0
D2	16.3	23.8 (28.1)	25.5	27.8	35.3
A3	18.7	24.5 (27.1)	27.3	28.7	30.0
B3	14.6	22.3 (25.8)	27.0	29.5	31.3
C3	12.8	22.2 (25.3)	25.5	27.0	32.0
D3	11.3	17.3 (19.7)	20.3	24.2	28.5

Note: 1. Values reported here are average of 3 specimens.

2. ** Values in () give results obtained using 150mm cubes. All other results are for 100mm cubes.

Table 5.2: Chloride penetration after continuous immersion in 3.5 % NaCl solution.

Mix	GGBS (%)	W/B ratio	Immers- ion Age (weeks)	Average depth of drilling & respective chloride concentrations (%)					
				5mm	10mm	15mm	20mm	25mm	
A1	0	0.4	6	0.102	0.042	0.011	0.004		
			12	0.179	0.089	0.042	0.021		
			24	0.212	0.113	0.049	0.037	0.014	
	35		6	0.057	0.015	0.010	0.005		
			12	0.129	0.036	0.017	0.008		
			24	0.185	0.058	0.021	0.012	0.005	
	55		6	0.060	0.019	0.009	0.005		
			12	0.095	0.041	0.010	0.006		
			24	0.175	0.088	0.019	0.008	0.005	
	75		6	0.077	0.019	0.012	0.005		
			12	0.080	0.034	0.014	0.010		
			24	0.134	0.061	0.015	0.008	0.005	
A2	0	0.5	6	0.210	0.112	0.032	0.008		
			12	0.179	0.076	0.029	0.012		
			24	0.531	0.367	0.166	0.091	0.062	
	35		6	0.214	0.076	0.025	0.007		
			12	0.131	0.058	0.020	0.006		
			24	0.405	0.359	0.159	0.039	0.010	
	55		6	0.064	0.026	0.011	0.005		
			12	0.143	0.038	0.013	0.008		
			24	0.216	0.109	0.022	0.017	0.006	
	75		6	0.089	0.052	0.018	0.005		
			12	0.123	0.047	0.019	0.006		
			24	0.141	0.056	0.015	0.005	0.004	
A3	0	0.6	6	0.275	0.169	0.022	0.006		
			12	0.381	0.243	0.134	0.054		
			24	0.417	0.326	0.223	0.135	0.109	
	35		6	0.143	0.068	0.036	0.009		
			12	0.172	0.081	0.044	0.009		
			24	0.392	0.216	0.188	0.045	0.013	
	55		6	0.244	0.102	0.066	0.011		
			12**	0.039	0.016	0.010	0.009		
			24	0.388	0.176	0.088	0.036	0.007	
	75		6	0.151	0.052	0.032	0.007		
			12	0.186	0.061	0.038	0.016		
			24	0.323	0.152	0.042	0.015	0.006	

** Values are exceptionally low, and not considered in further discussion.

Table 5.3: Chloride penetration after continuous immersion in 7.0% NaCl solution

Mix	GGBS (%)	W / B ratio	Immers-ion Age (weeks)	Average depth of drilling & respective chloride concentrations (%)				
				5mm	10mm	15mm	20mm	25mm
A1	0	0.4	6	0.097	0.046	0.019	0.005	
			12	0.166	0.083	0.036	0.012	
			24	0.384	0.256	0.176	0.078	0.025
B1	35	0.4	6	0.296	0.107	0.060	0.006	
			12	0.305	0.081	0.028	0.020	
			24	0.302	0.195	0.076	0.022	0.007
C1	55	0.4	6	0.212	0.075	0.027	0.009	
			12	0.310	0.113	0.029	0.013	
			24	0.329	0.141	0.035	0.015	0.006
D1	75	0.4	6	0.109	0.043	0.017	0.008	
			12	0.136	0.037	0.013	0.013	
			24	0.283	0.118	0.034	0.009	0.008
A2	0	0.5	6	0.368	0.147	0.109	0.042	
			12	0.380	0.186	0.119	0.079	
			24	0.520	0.252	0.291	0.118	0.082
B2	35	0.5	6	0.490	0.238	0.073	0.011	
			12	0.554	0.269	0.140	0.027	
			24	0.622	0.266	0.241	0.065	0.013
C2	55	0.5	6	0.322	0.102	0.049	0.009	
			12	0.342	0.165	0.035	0.015	
			24	0.426	0.173	0.097	0.024	0.009
D2	75	0.5	6	0.208	0.096	0.027	0.011	
			12	0.246	0.132	0.048	0.012	
			24	0.453	0.187	0.087	0.013	0.006
A3	0	0.6	6	0.411	0.172	0.134	0.062	
			12	0.506	0.250	0.160	0.139	
			24	0.728	0.481	0.378	0.287	0.199
B3	35	0.6	6	0.271	0.115	0.055	0.018	
			12	0.451	0.149	0.047	0.017	
			24	0.535	0.351	0.295	0.069	0.023
C3	55	0.6	6	0.268	0.107	0.035	0.009	
			12	0.342	0.139	0.053	0.017	
			24	0.467	0.194	0.069	0.023	0.015
D3	75	0.6	6	0.156	0.068	0.039	0.011	
			12	0.413	0.126	0.040	0.011	
			24	0.424	0.173	0.049	0.011	0.009

Table 5.4: Chloride penetration after exposure to alternate wetting and drying in NaCl solution, W/B ratio for above is 0.6

Mix	GGBS (%)	Solution concentration (%)	Exposure duration (weeks)	Average depth of drilling & respective chloride concentration (%)					
				5mm	10mm	15mm	20mm	25mm	
A3	0	3.5%	6	0.183	0.104	0.053	0.009		
			12	0.352	0.234	0.109	0.086		
			24	0.463	0.316	0.253	0.134	0.081	
	35		6	0.165	0.095	0.033	0.009		
			12	0.248	0.126	0.056	0.020		
			24	0.438	0.293	0.195	0.054	0.013	
C3	55		6	0.262	0.136	0.061	0.015		
			12	0.284	0.164	0.075	0.023		
			24	0.421	0.199	0.106	0.022	0.010	
	75		6	0.181	0.077	0.036	0.006		
			12	0.200	0.068	0.026	0.017		
			24	0.361	0.137	0.074	0.008	0.009	
A3	0	7.0%	6	0.271	0.165	0.093	0.042		
			12	0.385	0.239	0.159	0.108		
			24	0.735	0.449	0.367	0.207	0.163	
	35		6	0.220	0.143	0.053	0.019		
			12	0.332	0.173	0.066	0.022		
			24	0.680	0.387	0.244	0.063	0.018	
C3	55		6	0.321	0.216	0.106	0.032		
			12	0.484	0.215	0.098	0.026		
			24	0.638	0.314	0.172	0.053	0.021	
	75		6	0.262	0.148	0.040	0.011		
			12	0.320	0.213	0.052	0.023		
			24	0.535	0.241	0.189	0.042	0.016	

Table 5.5: Water soluble chloride at 6 week exposure in 3.5% NaCl solution

Mix	Drilling depth 5mm		Drilling depth 10mm		Drilling depth 15mm	
	Water soluble chloride (% by wt.)	% of sol. Chloride*	Water soluble chloride (% by wt.)	% of sol. Chloride*	Water soluble chloride (% by wt.)	% of sol. Chloride*
A1	0.091	0.89	0.037	0.88	0.085	0.88
B1	0.049	0.87	**	---	0.008	0.83
C1	0.054	0.90	0.016	0.87	**	---
D1	**	---	**	---	**	---
A2	0.165	0.79	0.105	0.96	0.027	0.85
B2	0.179	0.83	0.069	0.91	0.023	0.90
C2	0.053	0.83	0.023	0.94	**	---
D2	0.098	0.93	0.048	0.92	**	---
A3	0.235	0.85	0.151	0.89	0.021	0.95
B3	0.116	0.81	0.062	0.91	0.031	0.85
C3	0.201	0.82	0.092	0.90	0.052	0.83
D3	0.143	0.94	0.046	0.89	0.029	0.91

* Calculated w.r.t. corresponding total chlorides given in Table 5.2

** the results indicated here are ignored

Table 5.6: Water soluble chloride at 24 week exposure in 3.5% NaCl solution

Mix	Drilling depth 5mm		Drilling depth 10mm		Drilling depth 20mm	
	Water soluble chloride (% by wt.)	% of sol. Chloride*	Water soluble chloride (% by wt.)	% of sol. Chloride*	Water soluble chloride (% by wt.)	% of sol. Chloride*
A1	0.162	0.76	0.104	0.92	0.014	0.38
B1	0.117	0.63	0.022	0.39	0.011	0.94
C1	0.162	0.88	0.067	0.73	0.007	0.95
D1	**	---	0.024	0.40	**	---
A2	0.389	0.72	0.182	0.49	0.074	0.91
B2	0.232	0.57	0.206	0.57	0.037	0.95
C2	0.166	0.77	0.068	0.63	**	---
D2	0.117	0.82	0.048	0.85	**	---
A3	0.390	0.93	0.274	0.83	0.104	0.76
B3	0.349	0.87	0.197	0.91	0.032	0.71
C3	0.358	0.92	0.169	0.93	0.031	0.87
D3	0.313	0.95	0.148	0.89	**	---

* Calculated w.r.t. corresponding total chlorides given in Table 5.2

** The results indicated here are ignored

Table 5.7: Water soluble chloride at 24 week exposure in 7.0% NaCl solution

Mix	Drilling depth 5mm		Drilling depth 10mm		Drilling depth 20mm	
	Water soluble chloride (% by wt)	% of sol. Chloride*	Water soluble chloride (% by wt)	% of sol. Chloride*	Water soluble chloride (% by wt.)	% of sol. Chloride*
A1	0.304	0.76	0.163	0.63	0.042	0.49
B1	0.261	0.85	0.126	0.64	0.017	0.82
C1	0.292	0.88	0.101	0.71	**	---
D1	0.261	0.91	0.101	0.85	**	---
A2	0.357	0.68	0.195	0.77	0.102	0.89
B2	0.517	0.82	0.231	0.87	0.043	0.65
C2	0.338	0.78	0.144	0.82	0.019	0.79
D2	0.358	0.71	0.175	0.95	**	---
A3	0.577	0.79	0.330	0.67	0.221	0.74
B3	0.375	0.69	0.244	0.68	0.048	0.67
C3	0.411	0.86	0.182	0.92	0.016	0.78
D3	0.381	0.89	0.161	0.96	**	---

* Calculated w.r.t. corresponding total chlorides given in Table 5.3

** The results indicated here are ignored

Table 5.8 Compressive strength at different ages as % of 28 days strength

Mix	28 days strength (N/mm ²)	Strength as % of 28 days compressive strength				
		7 days	28 days	56 days	84 days	168 days
A1	35.3	83.7	100	104.2	106.2	119.0
B1	34.2	77.5	100	122.8	124.3	138.0
C1	31.8	72.3	100	115.7	117.9	123.2
D1	29.0	70.0	100	114.8	117.9	126.8
A2	30.4	78.0	100	110.2	114.5	120.1
B2	30.2	73.2	100	120.9	127.5	135.1
C2	27.6	63.4	100	110.1	115.2	141.3
D2	23.8	68.5	100	107.1	116.8	148.3
A3	24.5	76.3	100	111.4	117.1	122.4
B3	22.3	65.5	100	121.1	132.3	140.4
C3	22.2	57.7	100	114.9	121.6	144.1
D3	17.3	65.3	100	117.3	139.9	164.7

Table 5.9: Diffusion coefficient and surface concentration values obtained by curve fitting from data obtained after continuous immersion in 3.5% NaCl solution.

Mix	GGBS (%)	W/B ratio	Immersion Age (weeks)	Diffusion coefficient (D_{imm}) (10^{-8} cm^2/s)	' D_{imm} ' (% of 6 week value)	Surface concentration (C_s) (% by wt.)	' C_s ' (% of 6 week value)
A1	0	0.4	6	9.3	100	0.19	100
			12	6.3	68	0.16	84
			24	4.4	47	0.32	168
			6	7.7	100	0.11	100
			12	5.5	71	0.51	463
			24	1.9	24	0.37	336
C1	55	0.5	6	7.7	100	0.12	100
			12	3.5	45	0.44	366
			24	2.8	36	0.31	258
			6	6.8	100	0.16	100
			12	5.3	78	0.19	118
			24	2.6	38	0.24	150
A2	0	0.5	6	12.1	100	0.36	100
			12	5.5	45	0.31	86
			24	5.8	47	0.78	216
			6	8.4	100	0.41	100
			12	5.4	64	0.23	56
			24	5.8	69	0.63	153
C2	55	0.6	6	10.9	100	0.11	100
			12	3.2	29	0.31	281
			24	2.8	25	0.38	345
			6	13.9	100	0.15	100
			12	4.9	35	0.22	146
			24	2.3	16	0.26	173
B3	35	0.6	6	12.1	100	0.48	100
			12	11.4	94	0.55	114
			24	11.7	96	0.54	112
			6	13.8	100	0.23	100
			12	6.9	50	0.28	121
			24	6.0	43	0.55	239
C3	55	0.6	6	12.7	100	0.40	100
			12**	7.3	57	0.06	**
			24	3.3	26	0.63	157
			6	9.2	100	0.28	100
			12	4.7	51	0.34	121
			24	2.8	30	0.56	200

Table 5.10: Diffusion coefficient and surface concentration values obtained by curve fitting from data obtained after continuous immersion in 7.0% NaCl solution.

Mix	GGBS (%)	W/B ratio	Immersion Age (weeks)	Diffusion coefficient (D) (10^{-8} cm 2 /s)	'D _{imm} ' (% of 6 week value)	Surface concentration (C ₀) (% by wt)	'C _s ' (% of 6 week value)	
A1	0	0.4	6	12.7	100	0.16	100	
			12	6.9	54	0.27	168	
			24	7.0	55	0.54	337	
	35		6	9.4	100	0.54	100	
			12	3.2	34	0.66	122	
			24	4.3	45	0.48	88	
C1	55		6	8.2	100	0.41	100	
			12	4.1	50	0.60	146	
			24	2.4	29	0.60	146	
	75		6	10.6	100	0.19	100	
			12	3.3	31	0.29	152	
			24	2.4	23	0.52	273	
A2	0	0.5	6	12.7	100	0.60	100	
			12	10.4	81	0.53	88	
			24	8.3	65	0.67	111	
	35		6	11.2	100	0.86	100	
			12	6.6	58	0.91	105	
			24	5.2	46	0.92	106	
C2	55		6	8.2	100	0.62	100	
			12	5.2	63	0.62	100	
			24	3.1	37	0.70	112	
	75		6	10.4	100	0.37	100	
			12	7.0	67	0.40	108	
			24	2.7	25	0.79	213	
A3	0	0.6	6	13.8	100	0.65	100	
			12	11.5	83	0.69	106	
			24	13.6	98	0.87	133	
	35		6	10.9	100	0.47	100	
			12	4.4	40	0.82	174	
			24	6.8	52	0.76	161	
C3	55		6	9.2	100	0.50	100	
			12	5.1	55	0.61	122	
			24	2.5	27	0.84	168	
	75		6	12.7	100	0.26	100	
			12	3.4	26	0.87	334	
			24	2.3	18	0.79	303	

Table 5.11: Chloride penetration results after exposure to alternate wetting and drying in NaCl solution, W/B ratio for all mixes is 0.6

Mix	GGBS	Solution concentration (%)	Exposure duration (weeks)	Diffusion coefficient (D_{wd}) (10^{-8} cm ² /s)	' D_{wd} ' (% of 6 week value)	Surface concentration (C_0) (% by wt.)	' C_s ' (% of 6 week value)	
A3	0	3.5%	6	15.9	100	0.29	100	
			12	12.4	78	0.50	172	
			24	10.0	63	0.60	206	
	35		6	14.3	100	0.27	100	
			12	7.1	49	0.40	148	
			24	6.3	44	0.63	233	
	55		6	13.3	100	0.43	100	
			12	8.3	62	0.44	102	
			24	3.5	26	0.68	158	
D3	75	7.0%	6	11.4	100	0.31	100	
			12	4.2	36	0.38	122	
			24	2.5	21	0.65	209	
	0		6	17.2	100	0.43	100	
			12	15.8	91	0.51	118	
			24	10.0	58	0.92	213	
	35		6	17.7	100	0.34	100	
			12	6.7	37	0.55	161	
			24	4.9	27	1.01	297	
C3	55		6	17.2	100	0.50	100	
			12	6.2	36	0.80	160	
			24	4.7	27	0.94	188	
	75		6	12.1	100	0.45	100	
			12	7.8	64	0.52	115	
			24	4.4	36	0.79	175	

Table 5.12: Effect of GGBS proportion on chloride diffusivity and its variation with age: Diffusion coefficient values (D) in, $10^{-8} \text{ cm}^2/\text{s}$.

Immersion in 3.5% NaCl solution					Immersion in 7.0% NaCl solution				
Continuous immersion					Continuous immersion				
W/B ratio	Mix	Exposure duration (weeks)			W/B ratio	Mix	Exposure duration (weeks)		
		6	12	24			6	12	24
0.4	A1	9.3	6.3	4.4	0.4	A1	12.7	6.9	7.0
	B1	7.7	5.5	1.9		B1	9.4	3.2	4.3
	C1	7.7	3.5	2.8		C1	8.2	4.1	2.4
	D1	6.8	5.3	2.6		D1	10.6	3.3	2.4
	A2	12.1	5.5	5.8	0.5	A2	12.7	10.4	8.3
	B2	8.4	5.4	5.8		B2	11.2	6.6	5.2
	C2	10.9	3.2	2.8		C2	8.2	5.2	3.1
	D2	13.9	4.9	2.3		D2	10.4	7.0	2.7
0.6	A3	12.1	11.4	11.7	0.6	A3	13.8	11.5	13.6
	B3	13.8	6.9	6.0		B3	10.9	4.4	6.8
	C3	12.7	7.3	3.3		C3	9.2	5.1	2.5
	D3	9.2	4.7	2.8		D3	12.7	3.4	2.3
Wetting and drying exposure					Wetting and drying exposure				
0.6	A3	15.9	12.4	10.0	0.6	A3	17.2	15.8	10.0
	B3	14.3	7.1	6.3		B3	17.7	6.7	4.9
	C3	13.3	8.3	3.5		C3	17.2	6.2	4.7
	D3	11.4	4.2	2.5		D3	12.1	7.8	4.4

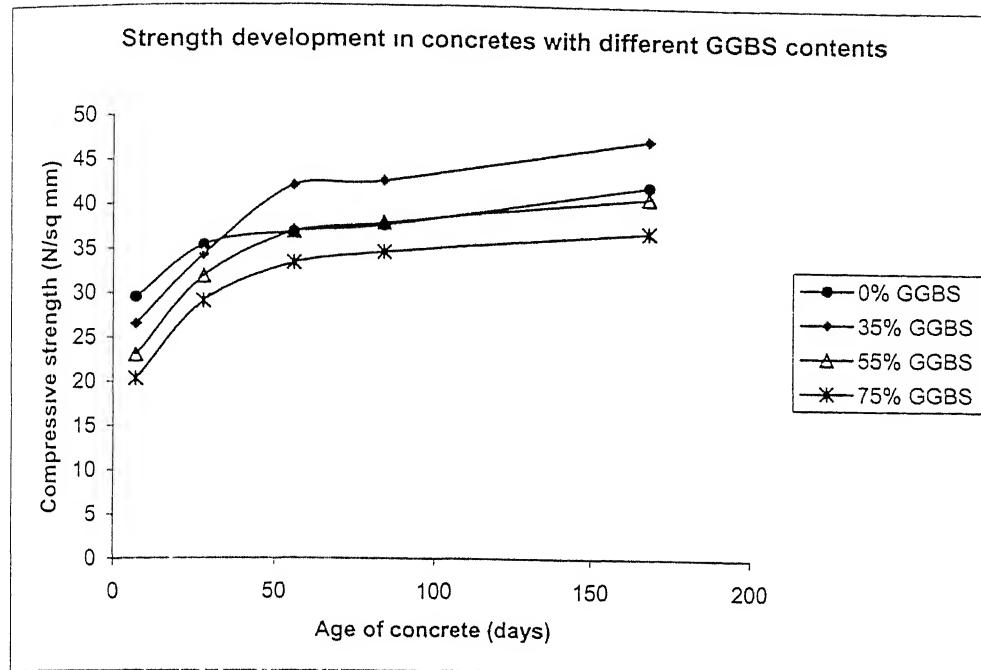


Figure 5.1: Strength development in concrete with W/B ratio 0.4

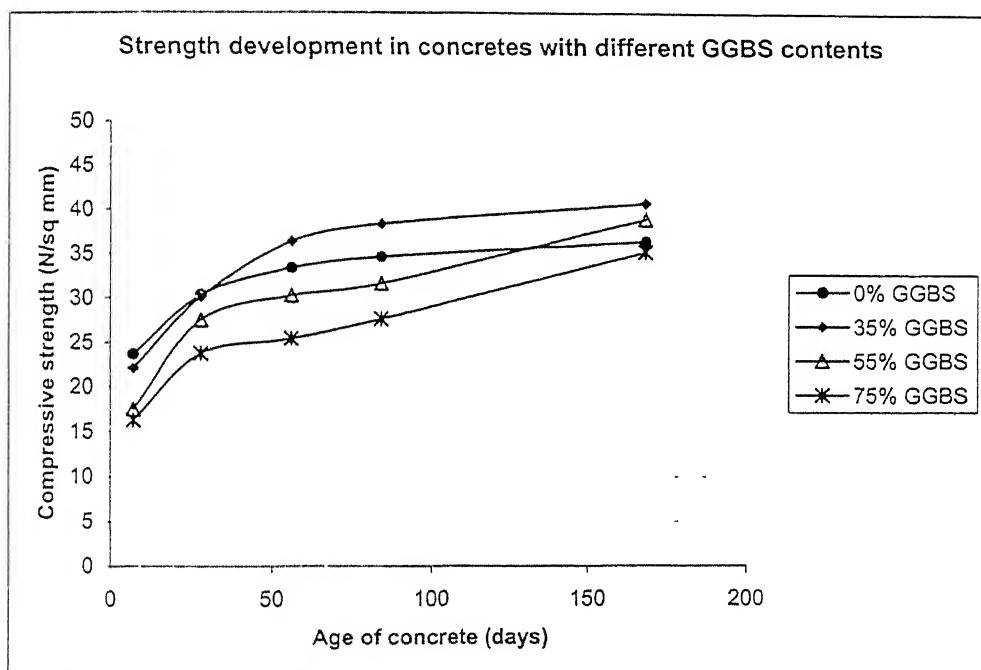


Figure 5.2: Strength development in concrete with W/B ratio 0.5

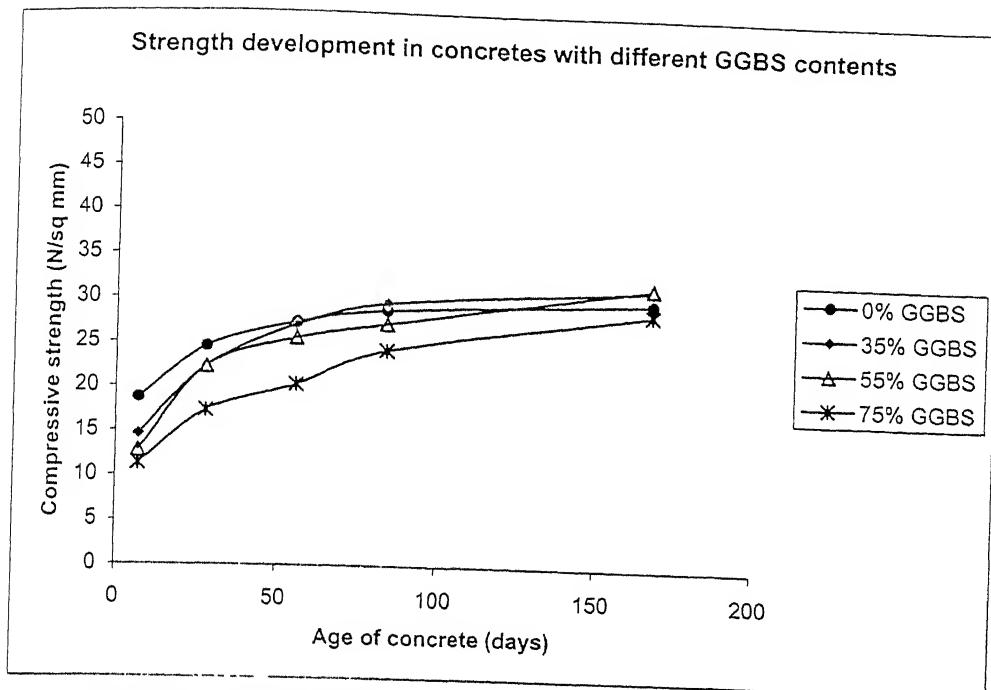


Figure 5.3: Strength development in concrete with W/B ratio 0.6

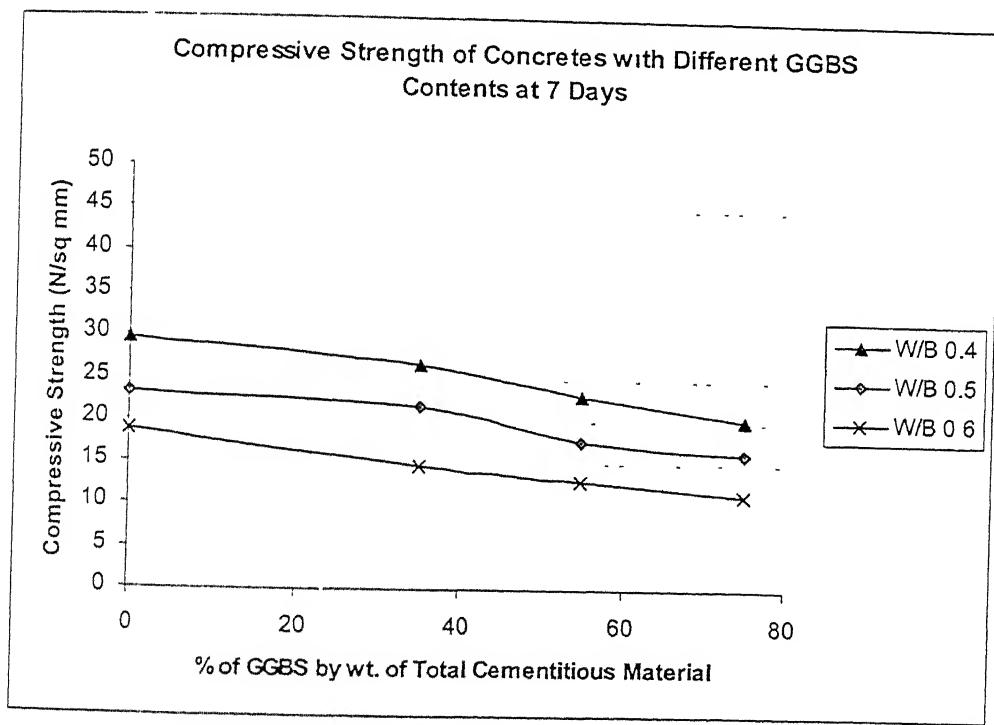


Figure 5.4: Compressive strength at 7 days

Compressive Strength of Concretes with Different GGBS Contents at 28 Days

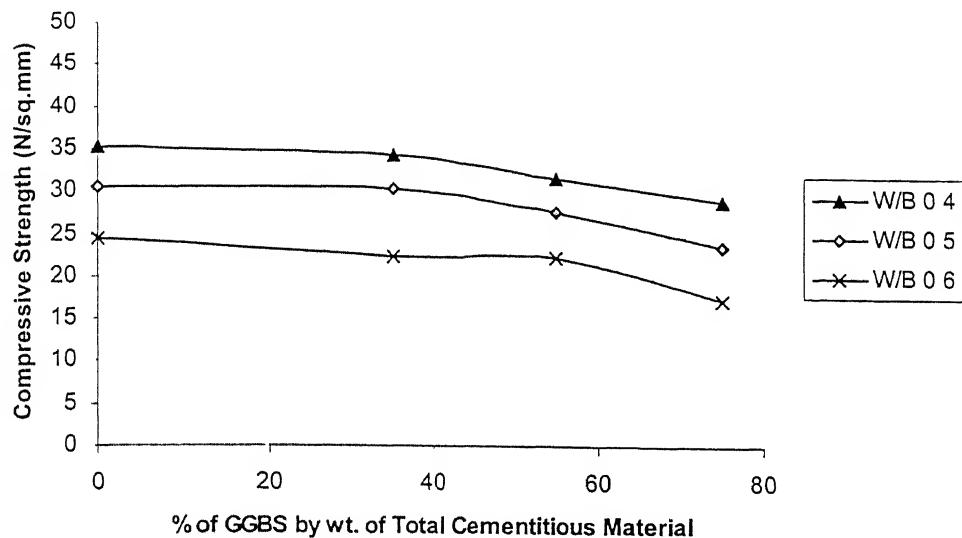


Figure 5.5: Compressive strength at 28 days

Compressive Strength of Concretes with Different GGBS Contents at 56 Days

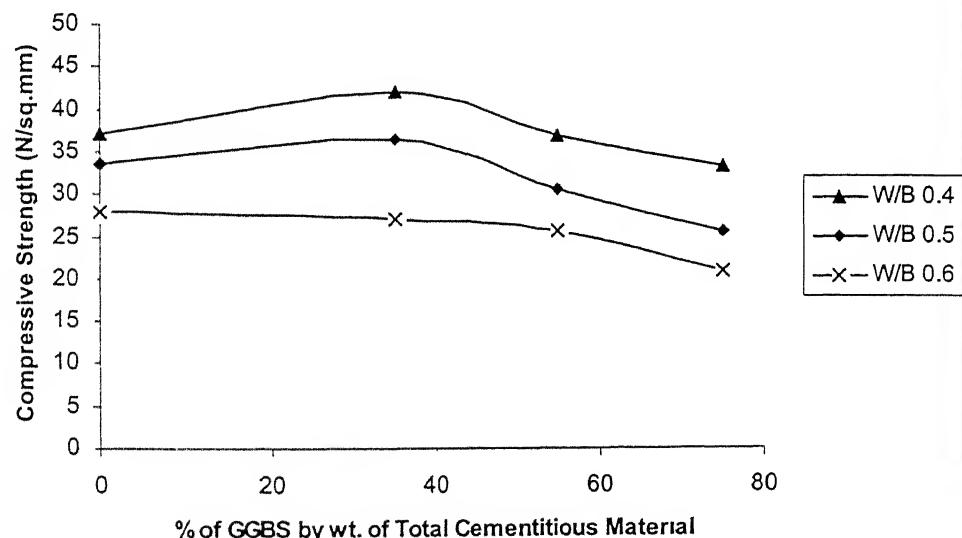


Figure 5.6: Compressive strength at 56 days

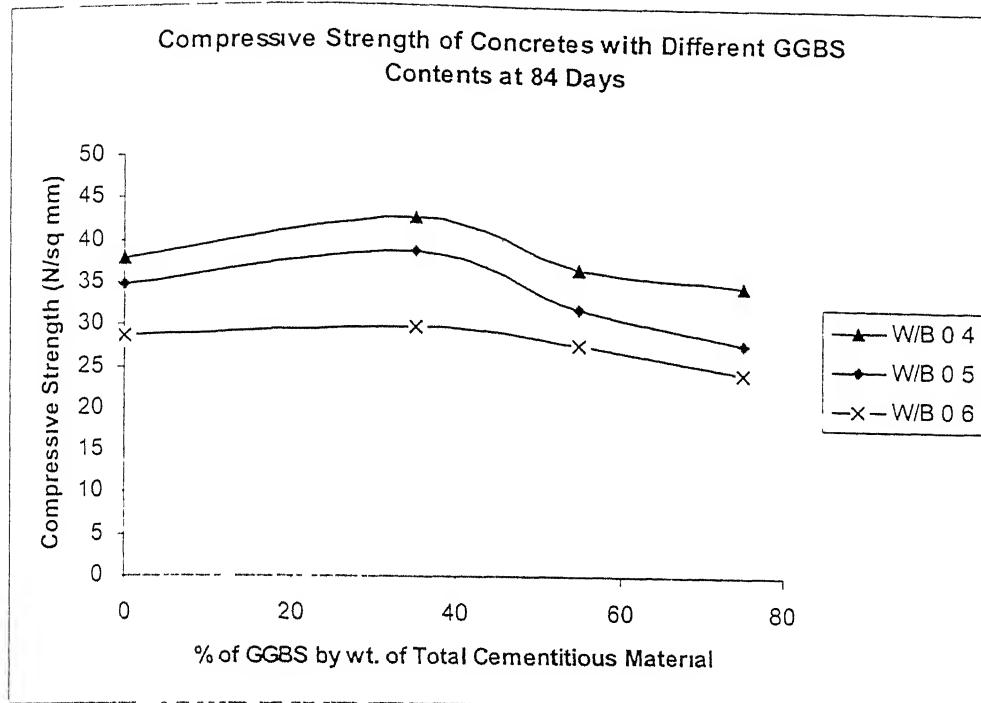


Figure 5.7: Compressive strength at 84 days

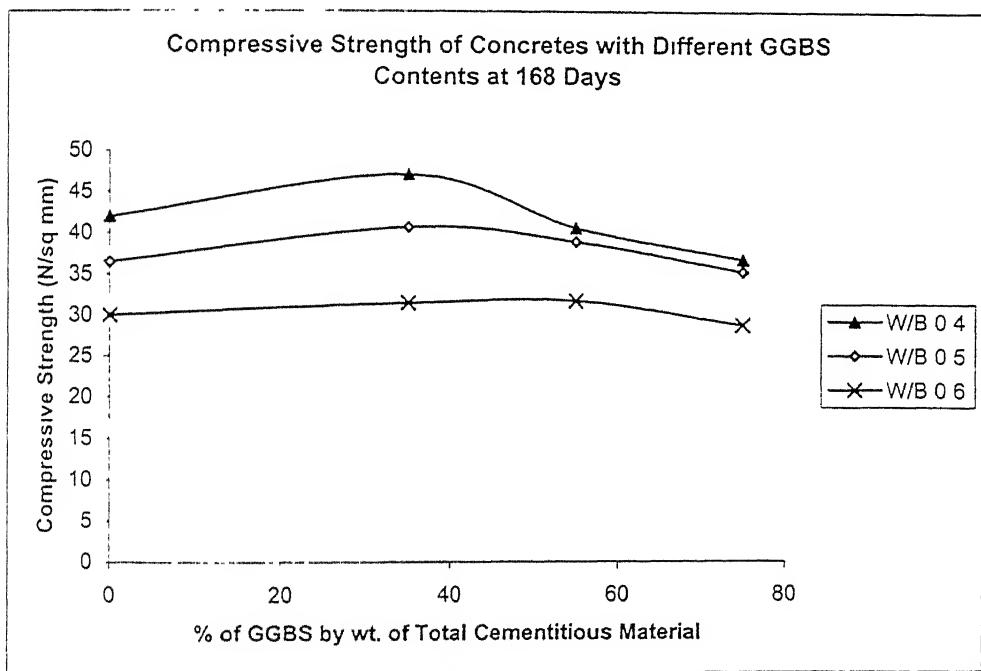


Figure 5.8: Compressive strength at 168 days

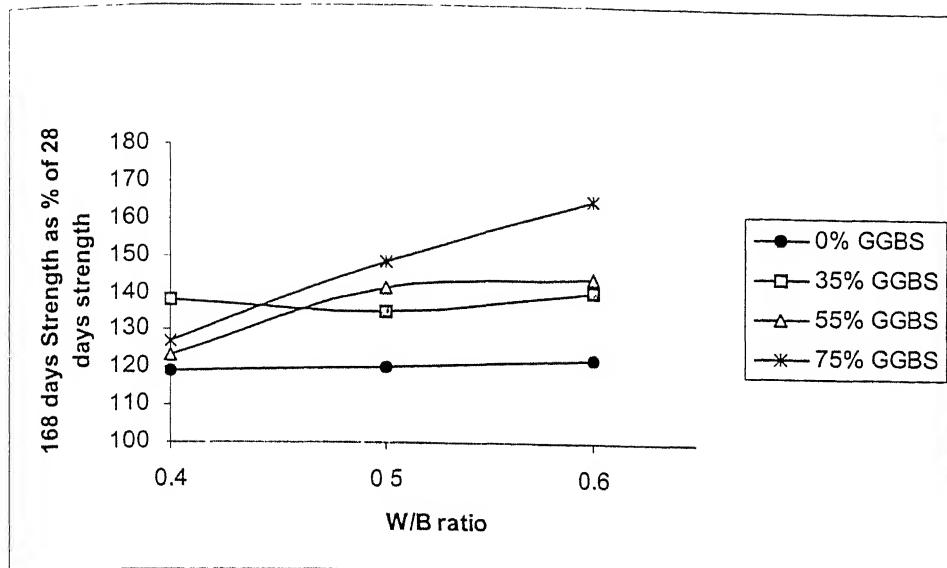


Figure 5.9: Percentage increase in compressive strength at 168 days for different replacement levels at different w/b ratios.

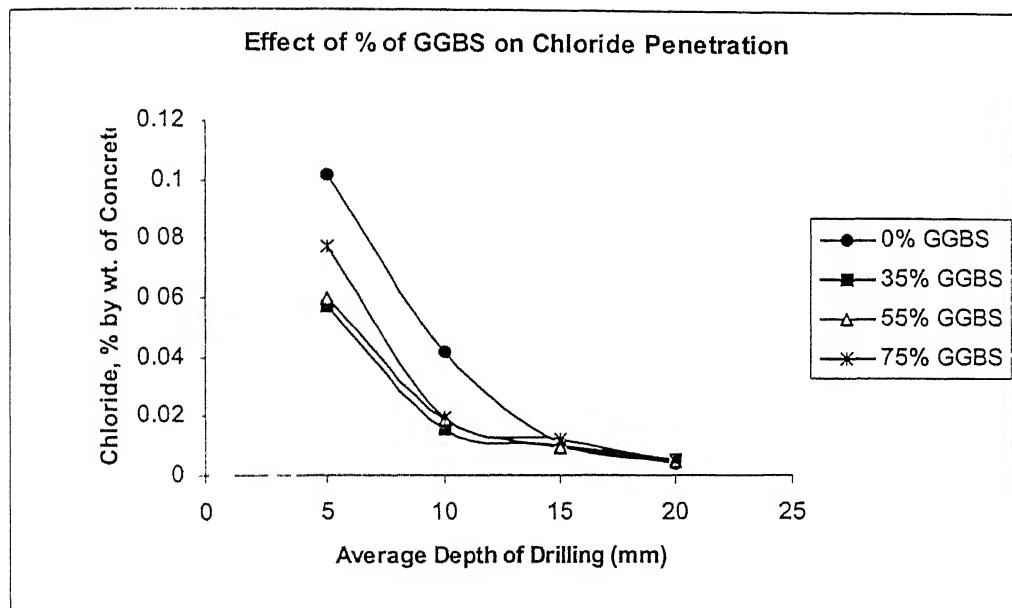


Figure 5.10: Chloride penetration in concrete of W/B ratio 0.4 after 6 week continuous immersion in 3.5% NaCl solution.

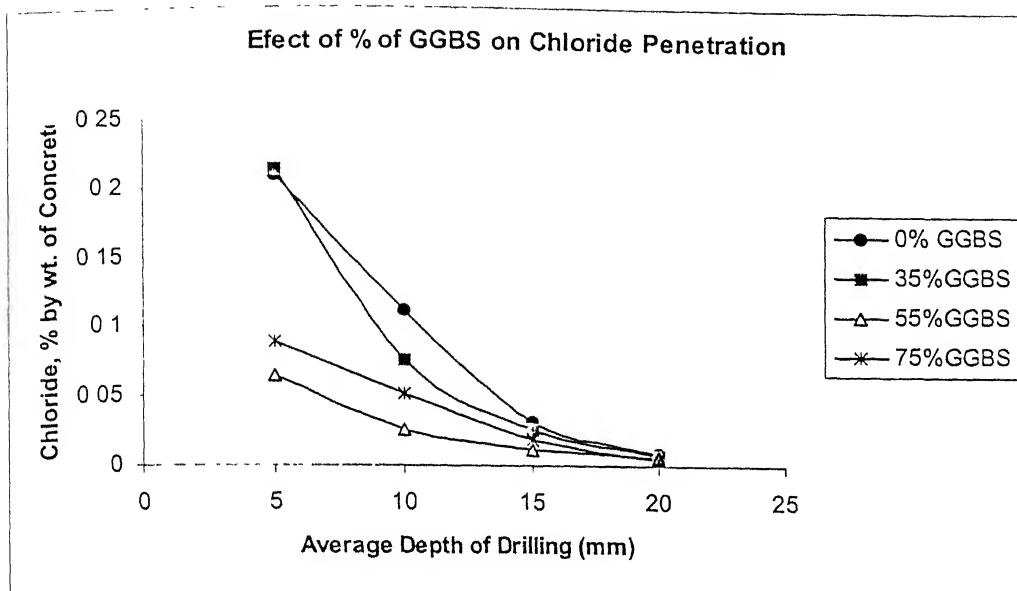


Figure 5.11. Chloride penetration in concrete of W/B ratio 0.5 after 6 week continuous immersion in 3.5% NaCl solution.

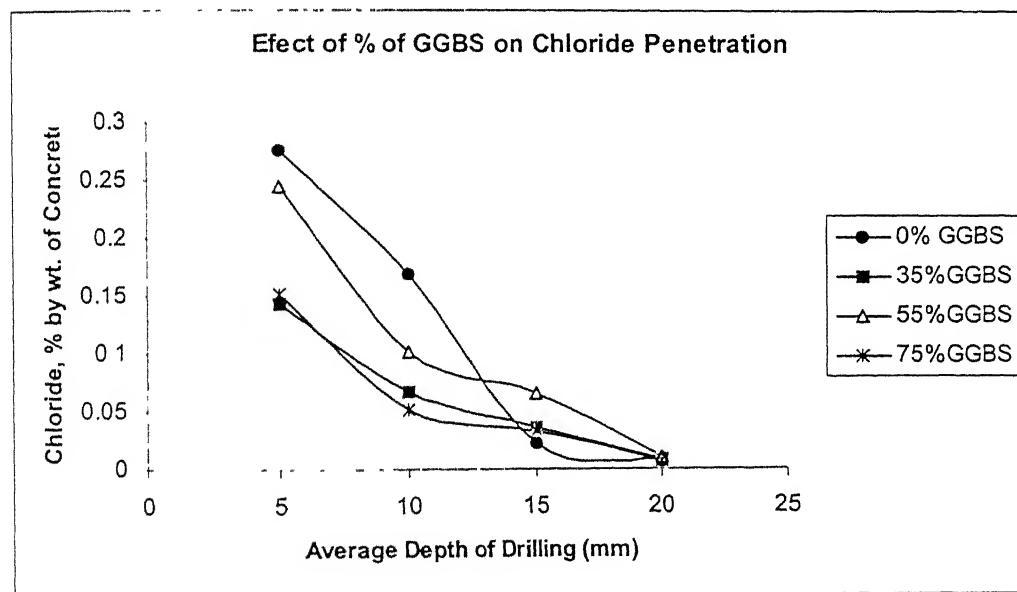


Fig. 5.12: Chloride penetration in concrete of W/B ratio 0.6 after 6 week continuous immersion in 3.5% NaCl solution.

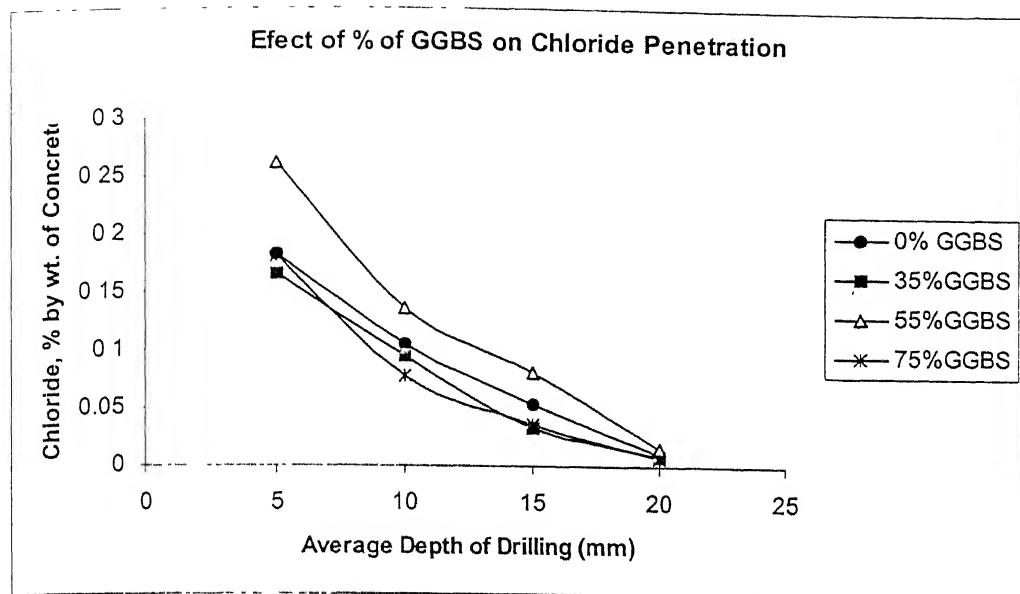


Figure 5.13: Chloride penetration in concrete of W/B ratio 0.6 after 6 weeks exposure to wetting and drying cycles in 3.5% NaCl solution.

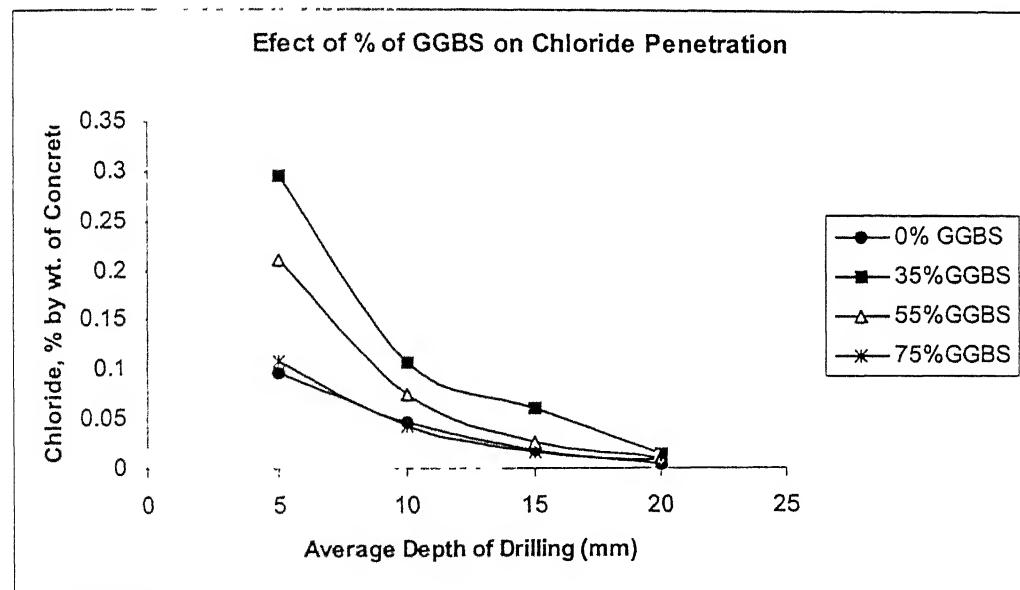


Figure 5.14: Chloride penetration in concrete of W/B ratio 0.4 after 6 week continuous immersion in 7.0% NaCl solution.

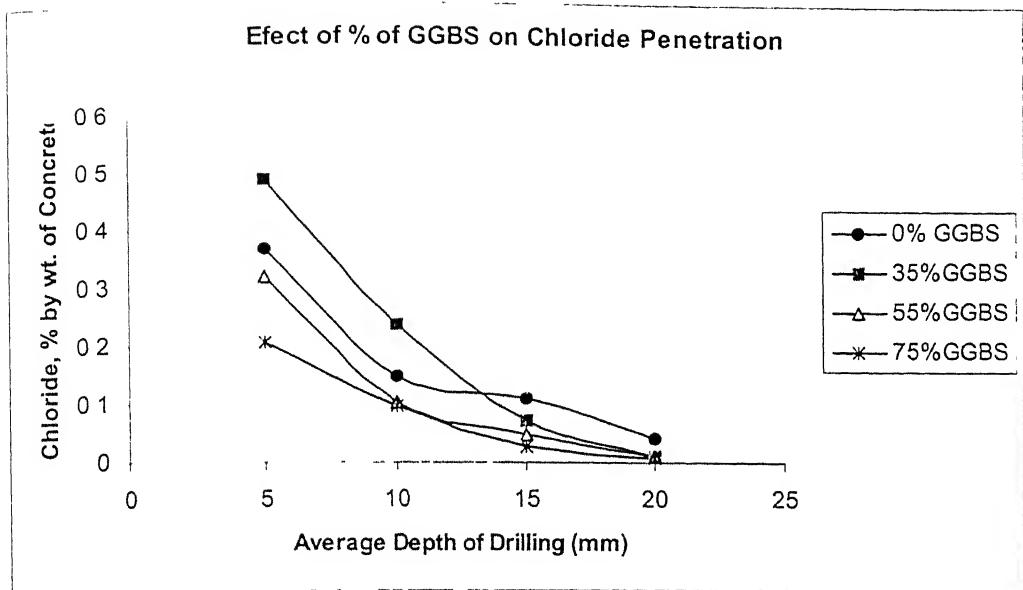


Figure 5.15: Chloride penetration in concrete of W/B ratio 0.5 after 6 weeks continuous immersion in 7.0% NaCl solution.

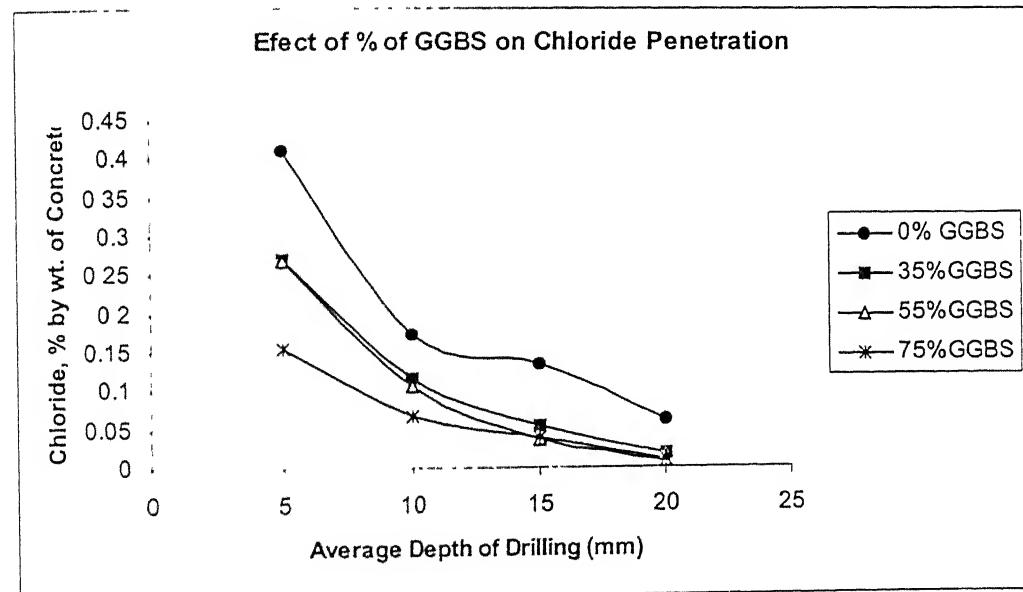


Figure 5.16: Chloride penetration in concrete of W/B ratio 0.6 after 6 week continuous immersion in 7.0% NaCl solution.

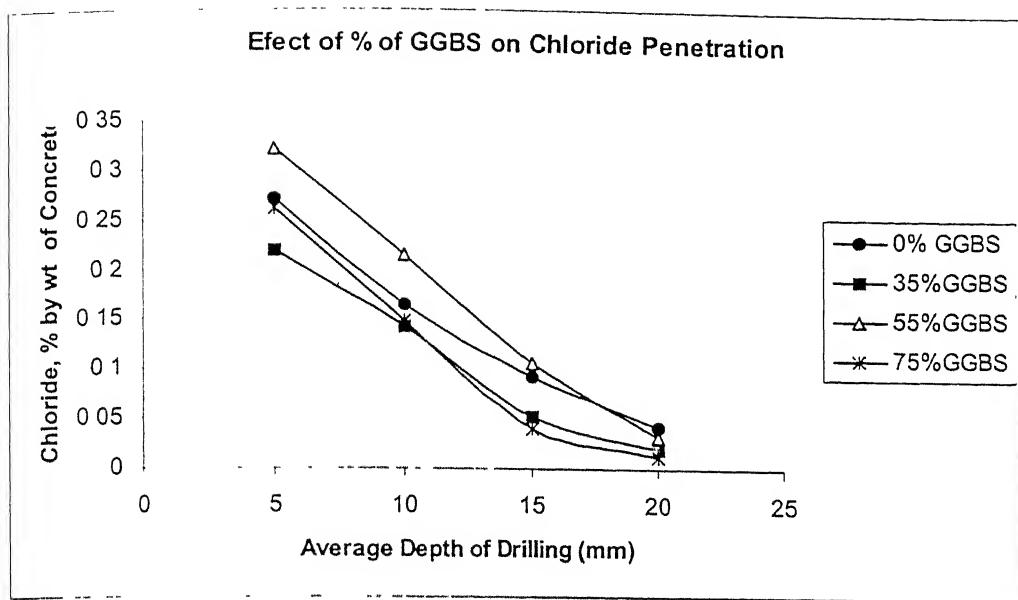


Figure 5.17: Chloride penetration in concrete of W/B ratio 0.6 after 6 weeks exposure to wetting and drying cycles in 7.0% NaCl solution.

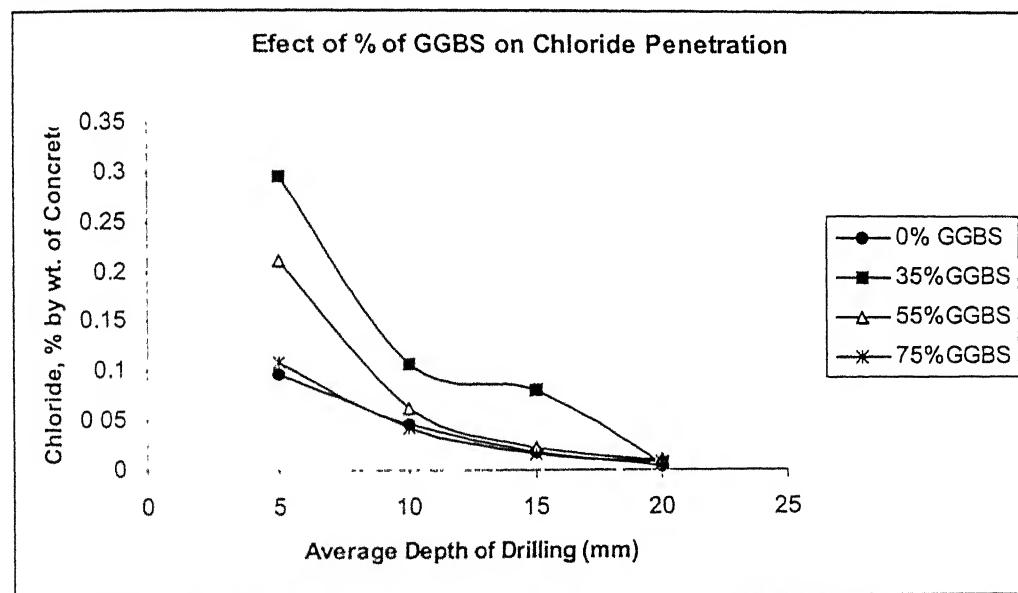


Figure 5.18: Chloride penetration in concrete of W/B ratio 0.4 after 12 weeks continuous immersion in 3.5% NaCl solution.

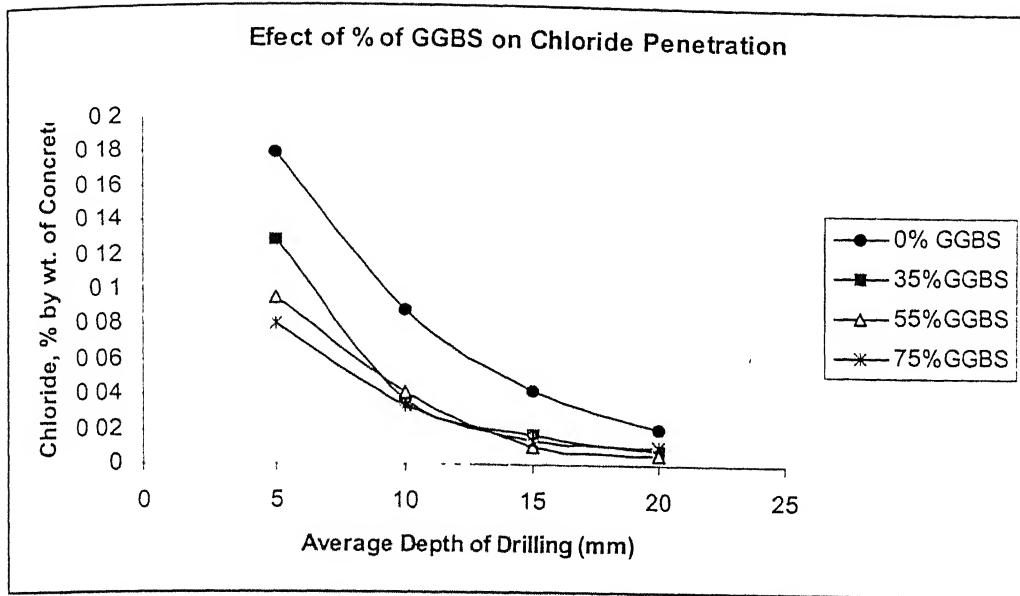


Figure 5.19: Chloride penetration in concrete of W/B ratio 0.5 after 12 weeks continuous immersion in 3.5% NaCl solution.

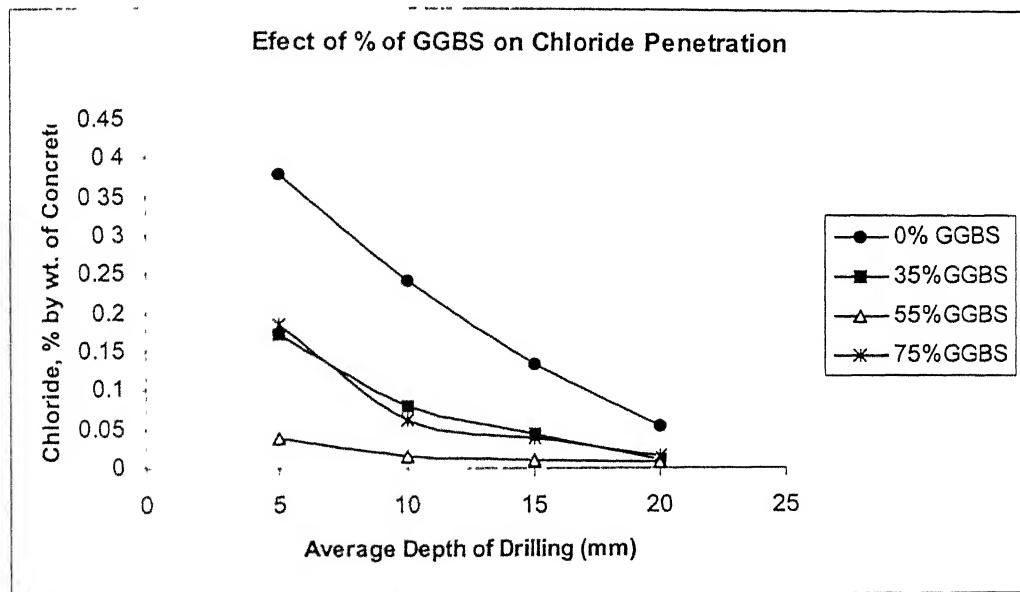


Figure 5.20: Chloride penetration in concrete of W/B ratio 0.6 after 12 week continuous immersion in 3.5% NaCl solution.

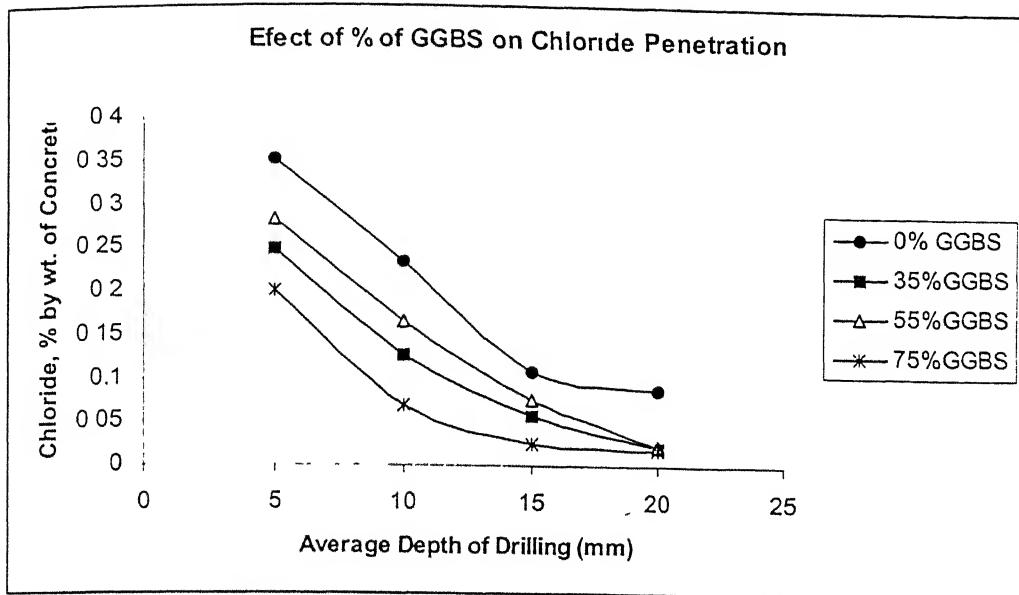


Figure 5.21: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks exposure to wetting and drying cycles in 3.5% NaCl solution.

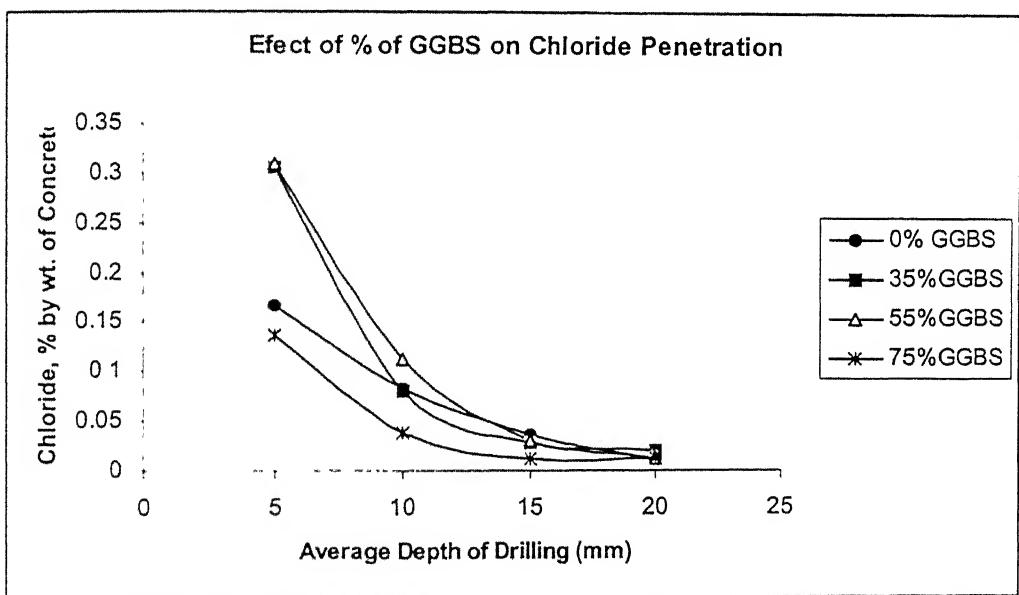


Figure 5.22: Chloride penetration in concrete of W/B ratio 0.4 after 12 week continuous immersion in 7.0% NaCl solution.

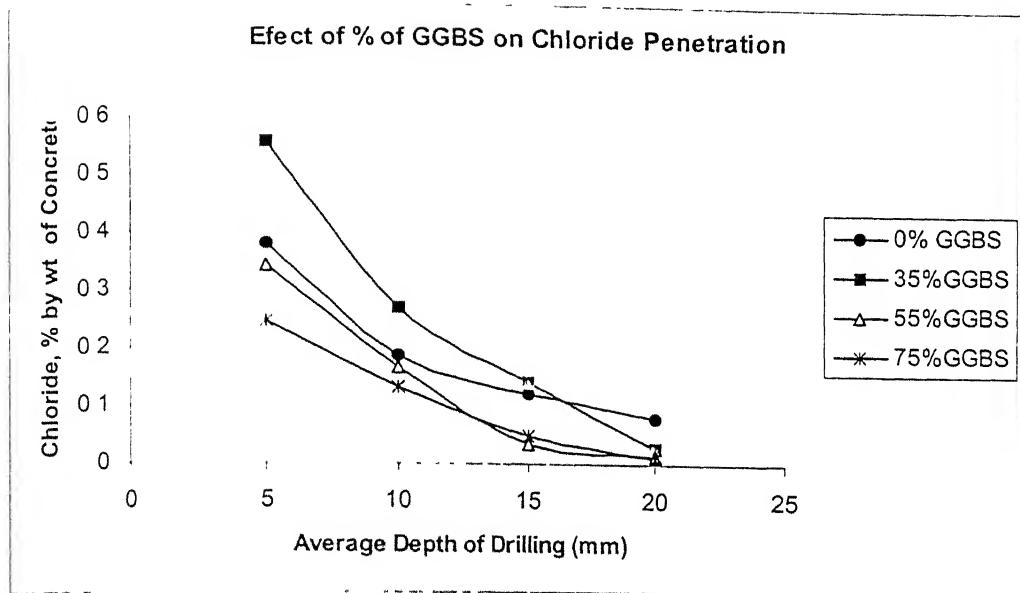


Figure 5.23: Chloride penetration in concrete of W/B ratio 0.5 after 12 weeks continuous immersion in 7.0% NaCl solution.

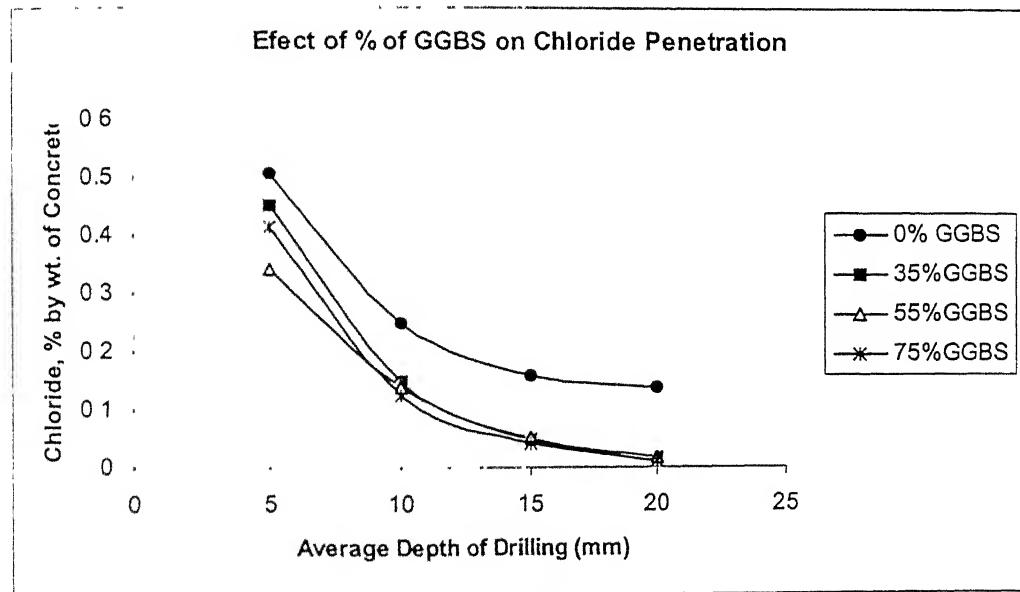


Figure 5.24: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks continuous immersion in 7.0% NaCl solution.

Effect of % of GGBS on Chloride Penetration

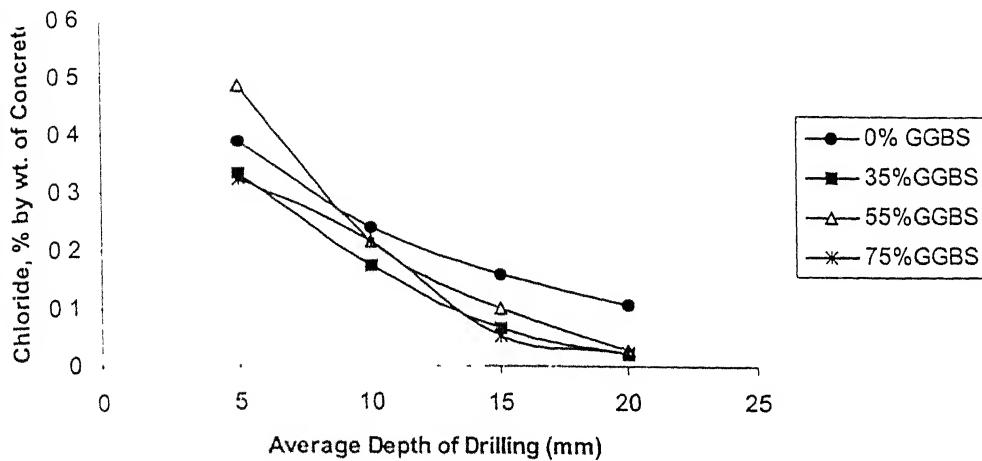


Figure 5.25: Chloride penetration in concrete of W/B ratio 0.6 after 12 weeks exposure to wetting and drying cycles in 7.0% NaCl solution.

Effect of % of GGBS on Chloride Penetration

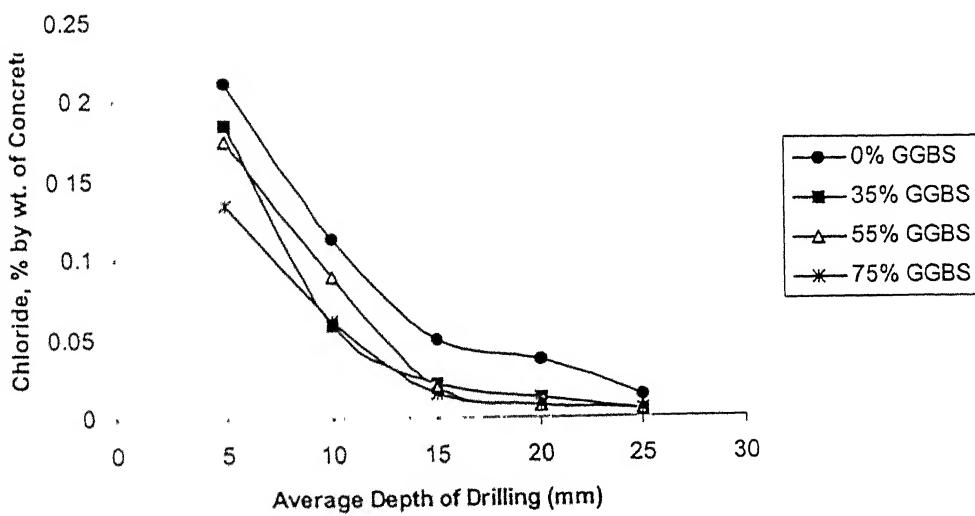


Figure 5.26: Chloride penetration in concrete of W/B ratio 0.4 after 24 weeks continuous immersion in 3.5% NaCl solution.

Effect of % of GGBS on Chloride Penetration

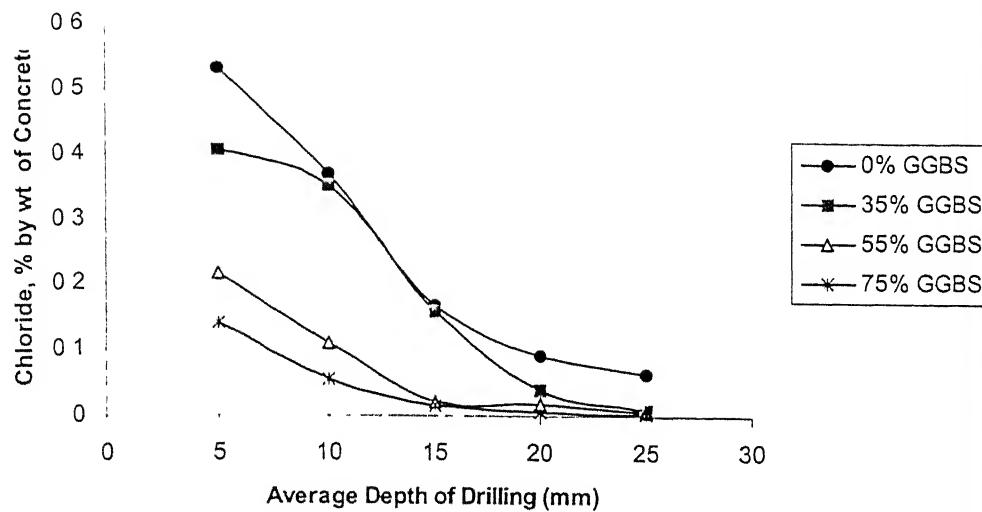


Figure 5.27: Chloride penetration in concrete of W/B ratio 0.5 after 24 weeks continuous immersion in 3.5% NaCl solution.

Effect of % of GGBS on Chloride Penetration

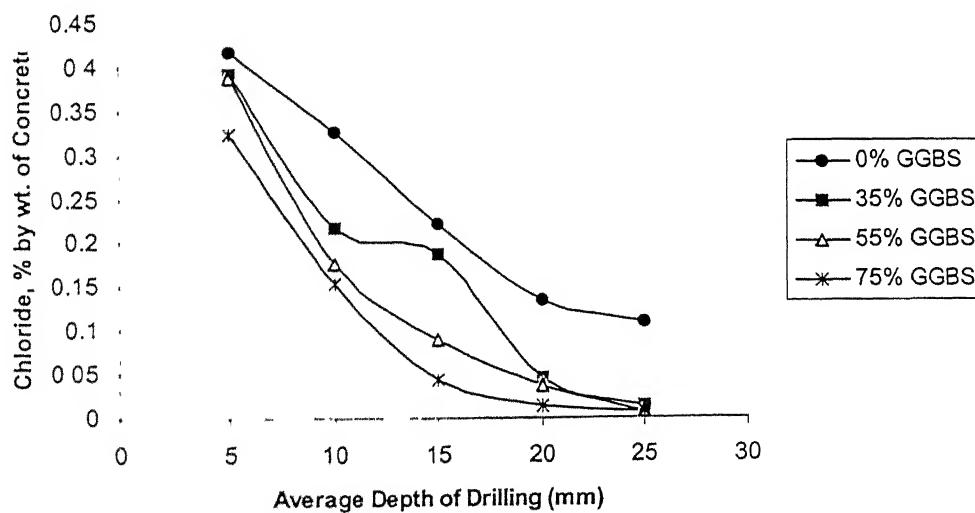


Figure 5.28: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks continuous immersion in 3.5% NaCl solution.

Effect of % of GGBS on Chloride Penetration

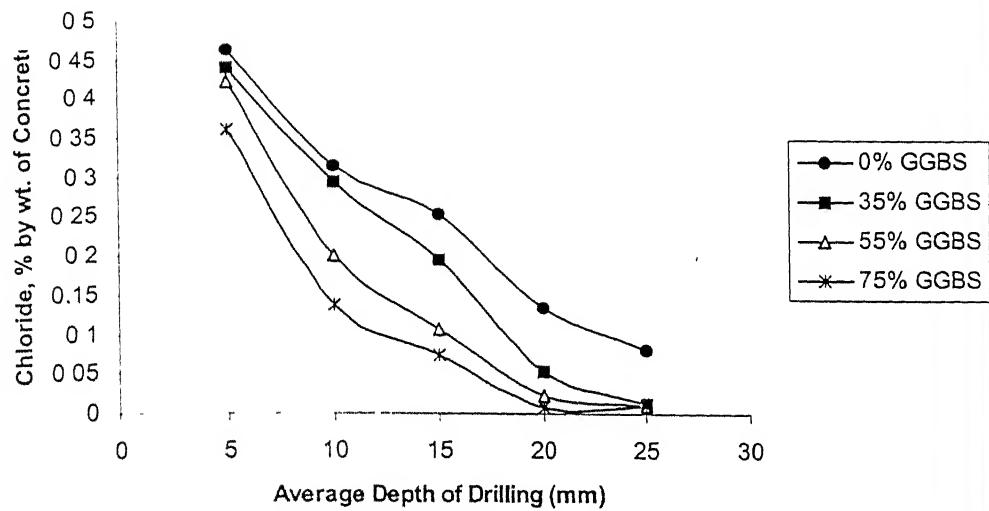


Figure 5.29: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks exposure to wetting and drying cycles in 3.5% NaCl solution.

Effect of % of GGBS on Chloride Penetration

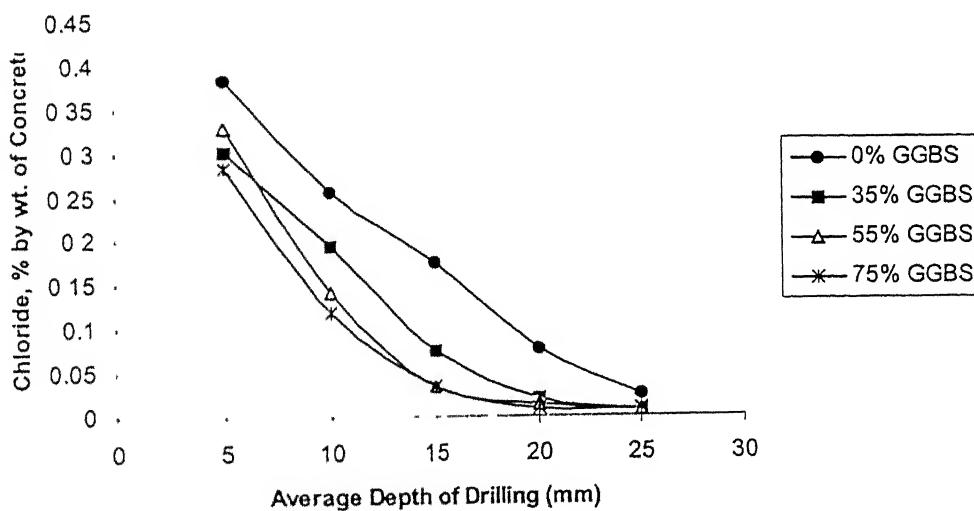


Figure 5.30: Chloride penetration in concrete of W/B ratio 0.4 after 24 weeks continuous immersion in 7.0% NaCl solution.

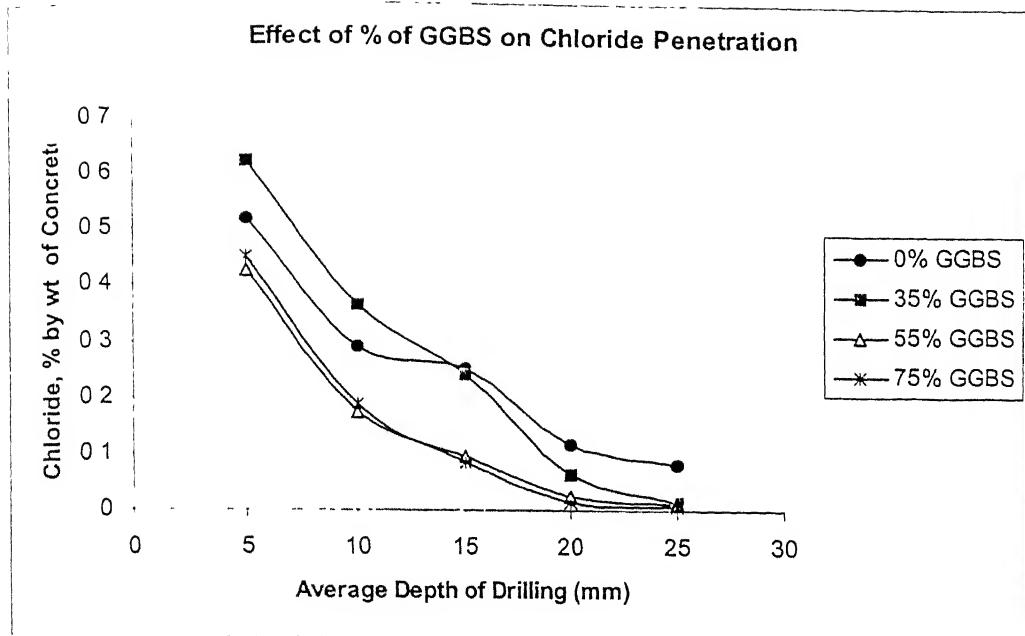


Figure 5.31: Chloride penetration in concrete of W/B ratio 0.5 after 24 weeks continuous immersion in 7.0% NaCl solution.

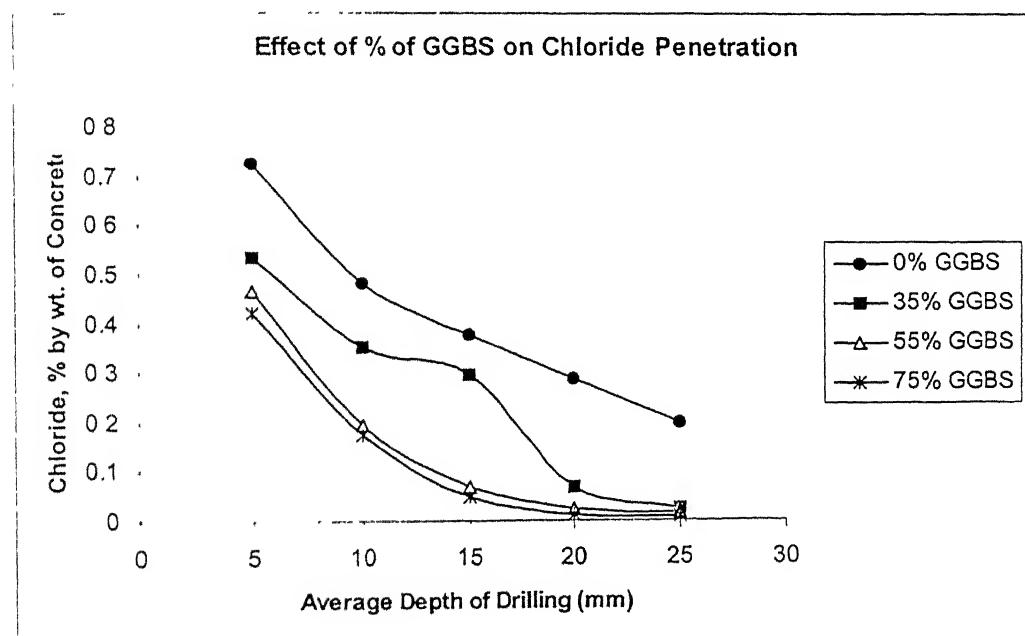


Figure 5.32: Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks continuous immersion in 7.0% NaCl solution.

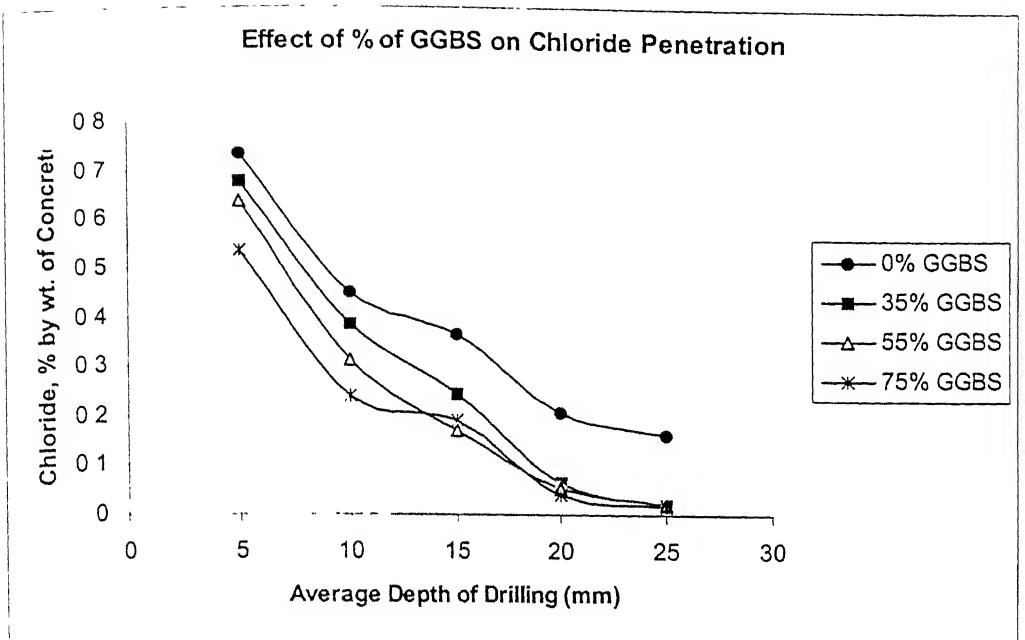


Figure 5.33. Chloride penetration in concrete of W/B ratio 0.6 after 24 weeks exposure to wetting and drying cycles in 7.0% NaCl solution.

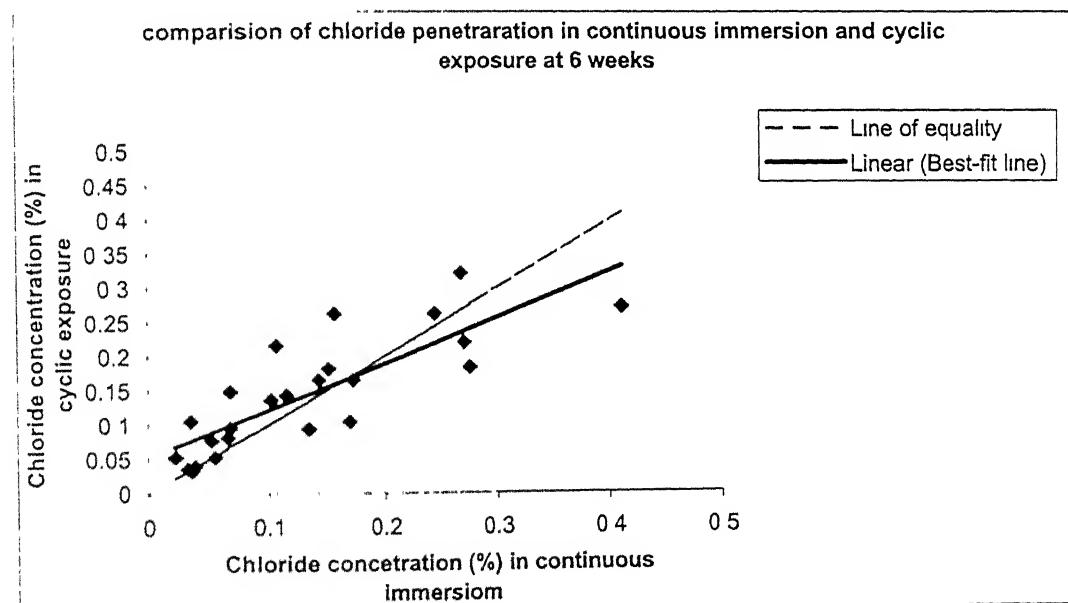


Figure 5.34: Effect of cyclic exposure on chloride penetration

comparison of chloride penetraration in continuous immersion and cyclic exposure at 12 weeks

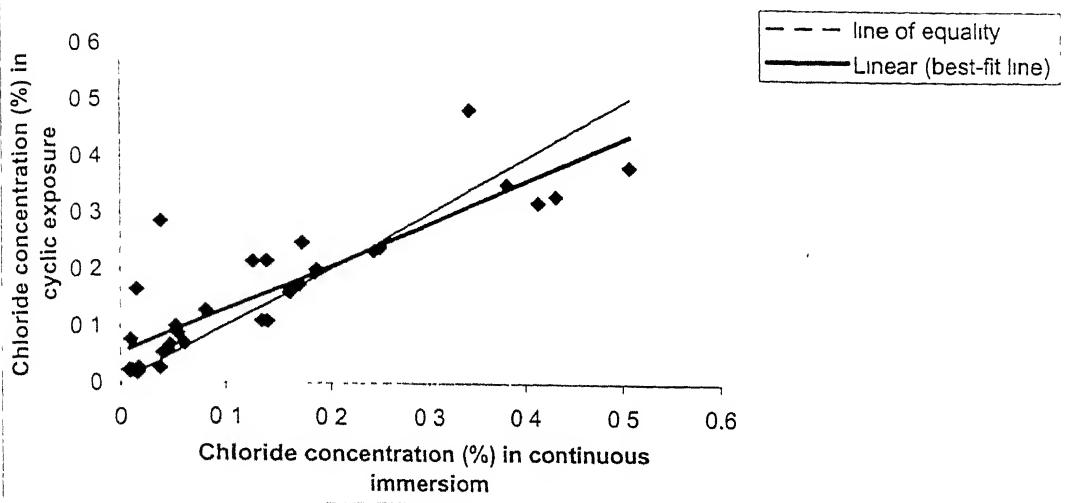


Figure 5.35: Effect of cyclic exposure on chloride penetration

comparison of chloride penetraration in continuous immersion and cyclic exposure at 24 weeks

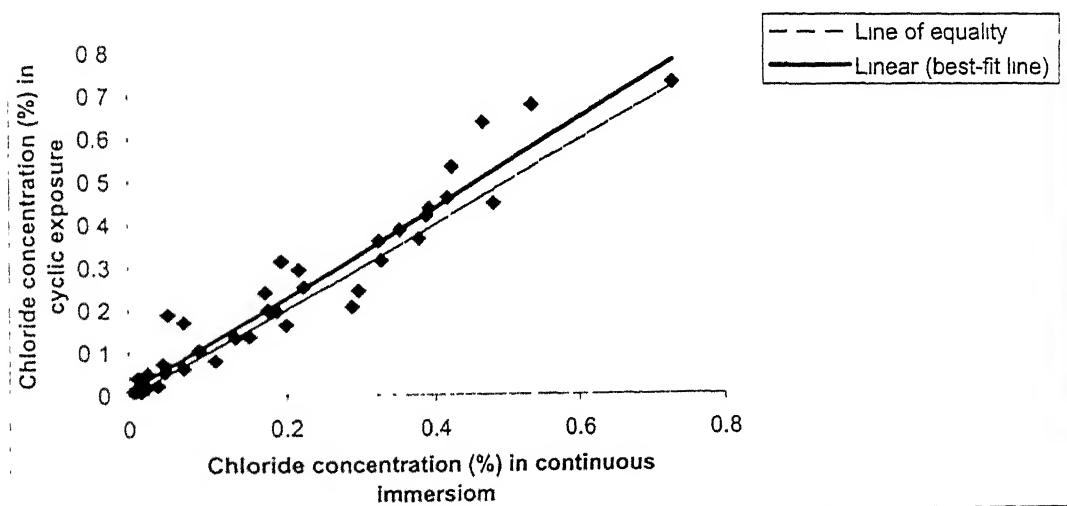


Figure 5.36: Effect of cyclic exposure on chloride penetration

Ratio of soluble chloride to total chloride at 6 weeks

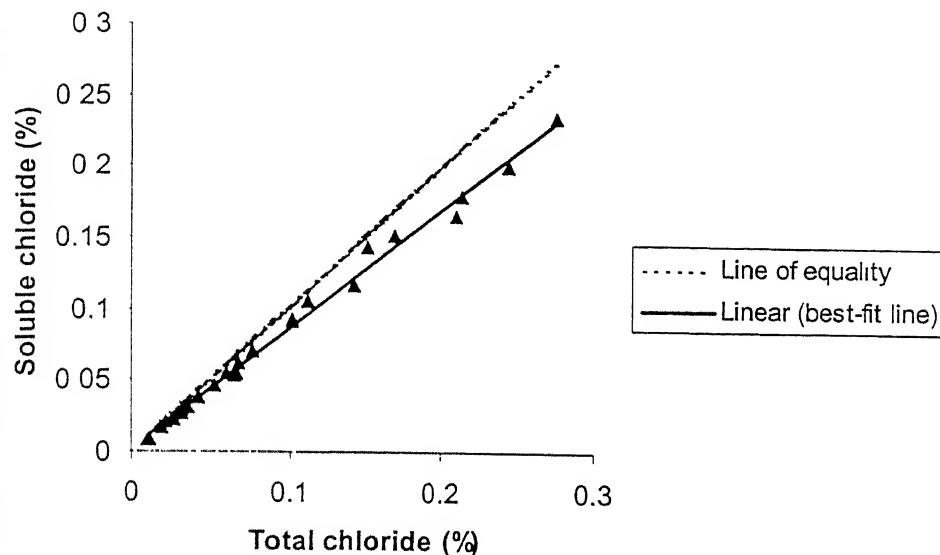


Figure 5.37: Immersion in 3.5% NaCl solution

Ratio of soluble chloride to total chloride at 24 weeks

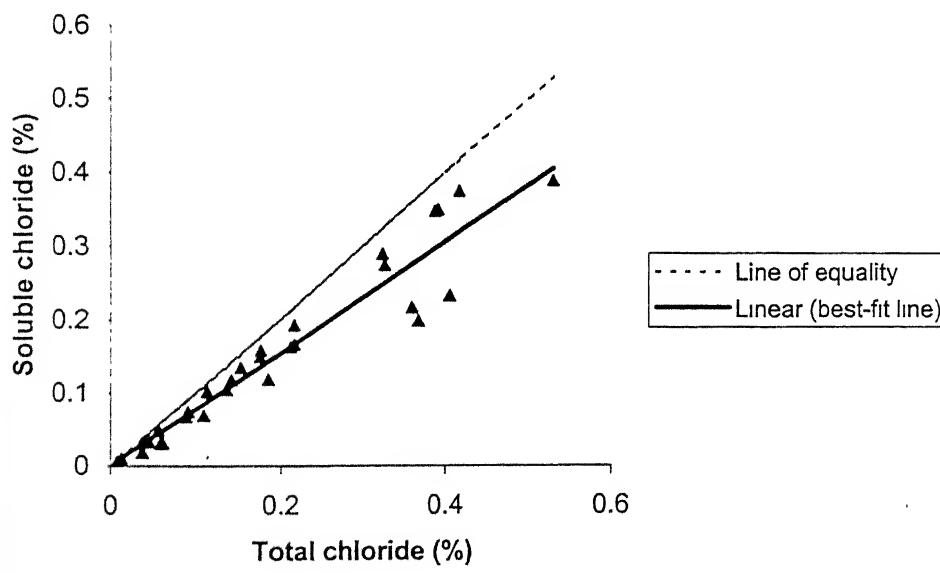


Figure 5.38: Exposure to 3.5% NaCl solution

Ratio of soluble chloride to total chloride at 24 weeks

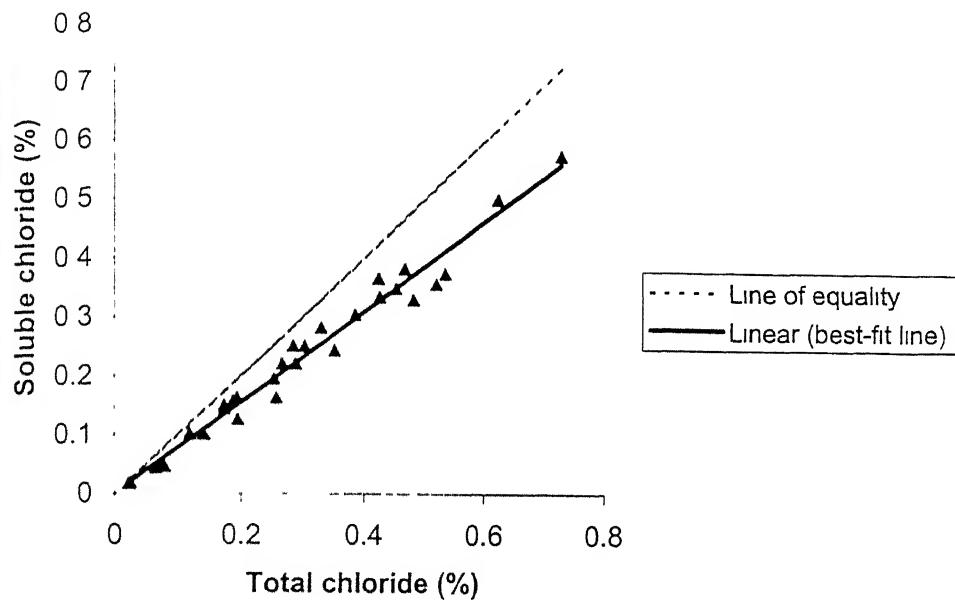


Figure 5.39: Exposure to 7.0% NaCl solution

Comparison of total and soluble chloride at 6 and 24 weeks

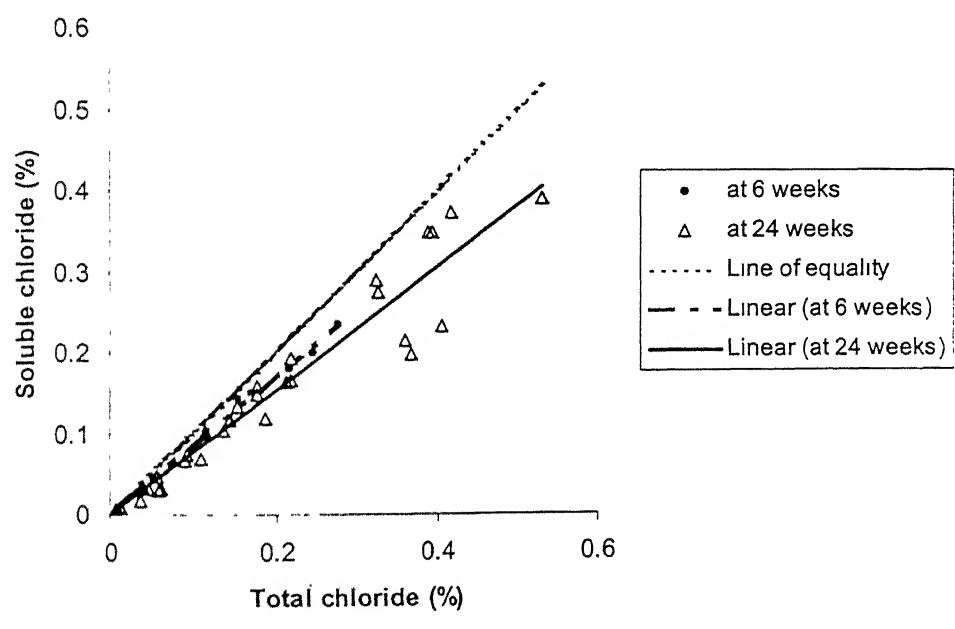


Figure 5.40: Exposure to 3.5% NaCl solution

Effect of exposure concentration on D_{app}

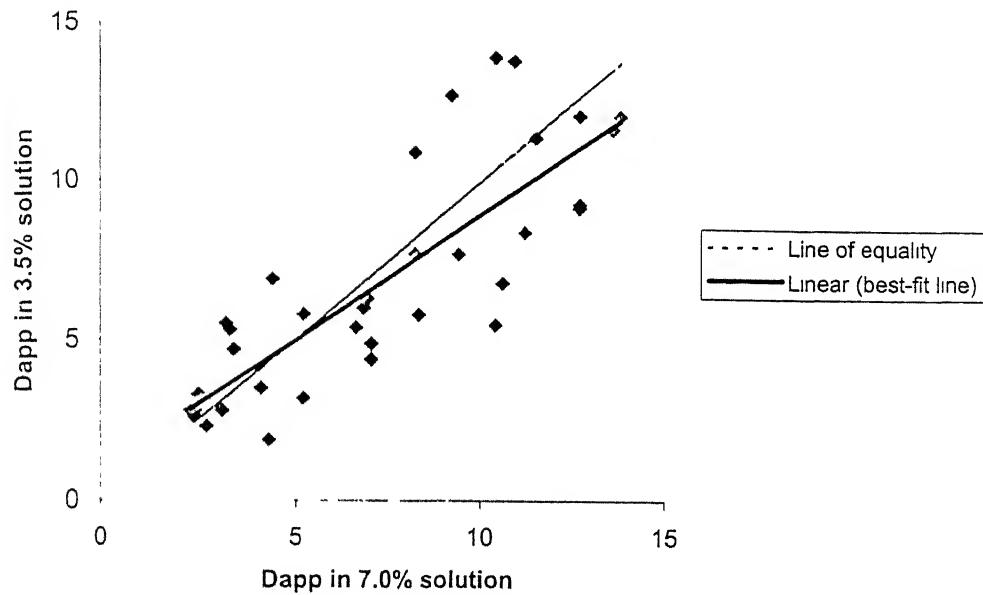


Figure 5.41: Effect of concentration of immersion solution on apparent diffusion coefficient (D_{app}), D_{app} is in $10^{-8} \cdot \text{cm}^2/\text{s}$

Effect of exposure concentration on C_s

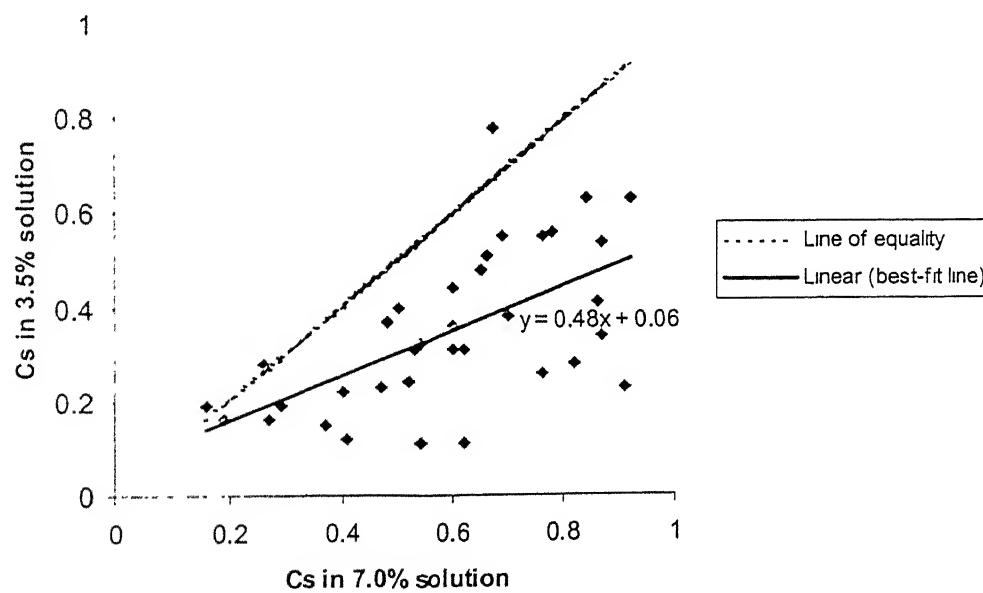


Figure 5.42: Effect of concentration of immersion solution on equilibrium surface concentration (C_s), C_s is in % by weight of concrete

Comparision of apparent diffusion coefficient 'Dapp' for continuous immersion and cyclic exposure at 6 weeks

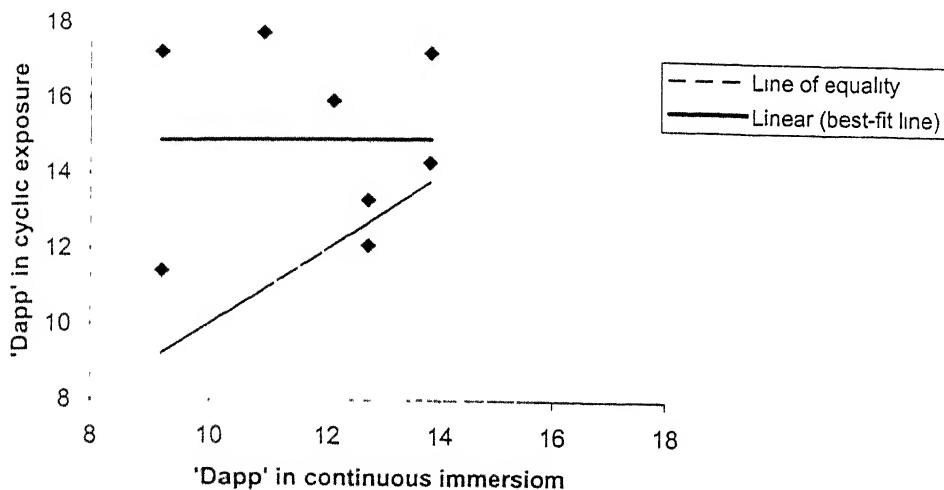


Figure 5.43: Effect of cyclic exposure on apparent diffusion coefficient, $'D_{app}'$ values are in $10^{-8} \cdot \text{cm}^2/\text{s}$

Comparision of apparent diffusion coefficient 'Dapp' for continuous immersion and cyclic exposure at 12 weeks

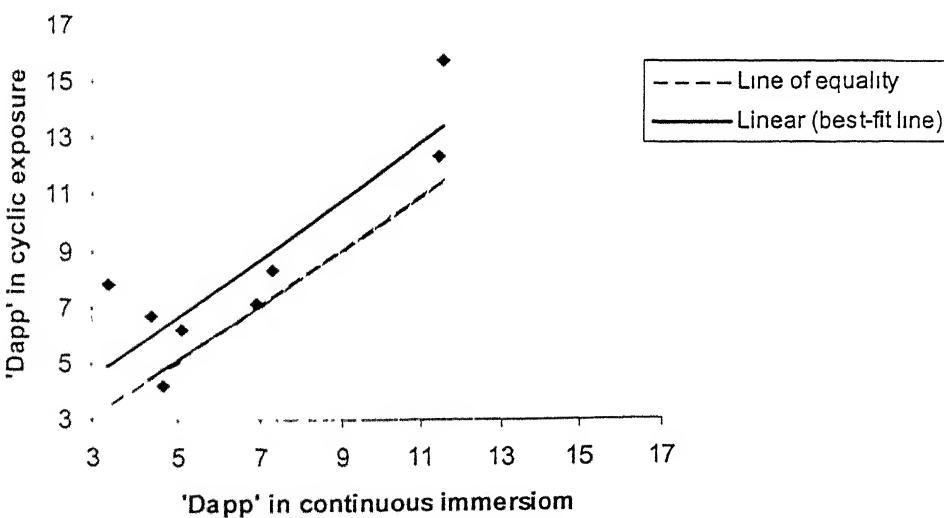


Figure 5.44: Effect of cyclic exposure on apparent diffusion coefficient, $'D_{app}'$ values are in $10^{-8} \cdot \text{cm}^2/\text{s}$

Comparision of apparent diffusion coefficient 'Dapp' for continuous immersion and cyclic exposure at 24 weeks

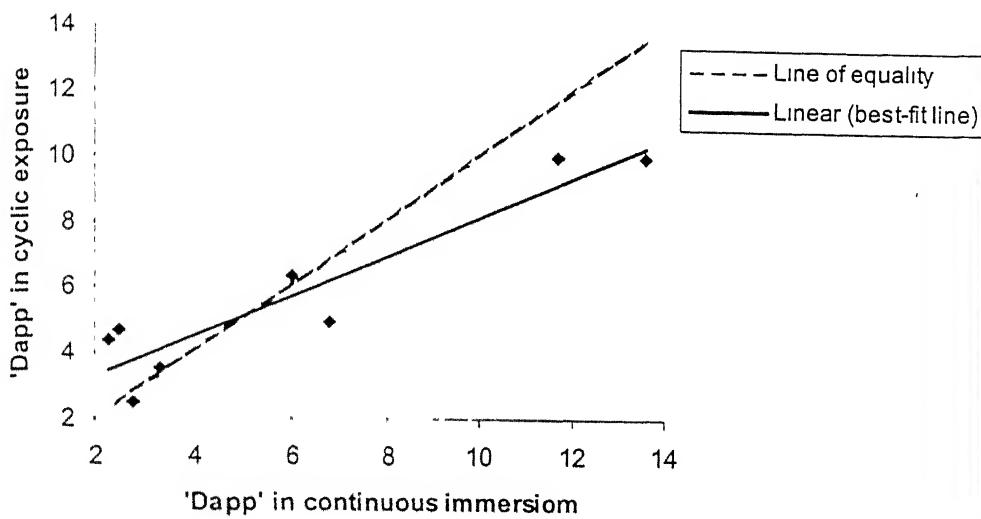


Figure 5.45: Effect of cyclic exposure on apparent diffusion coefficient, ' D_{app} ' values are in $10^{-8} \cdot \text{cm}^2/\text{s}$

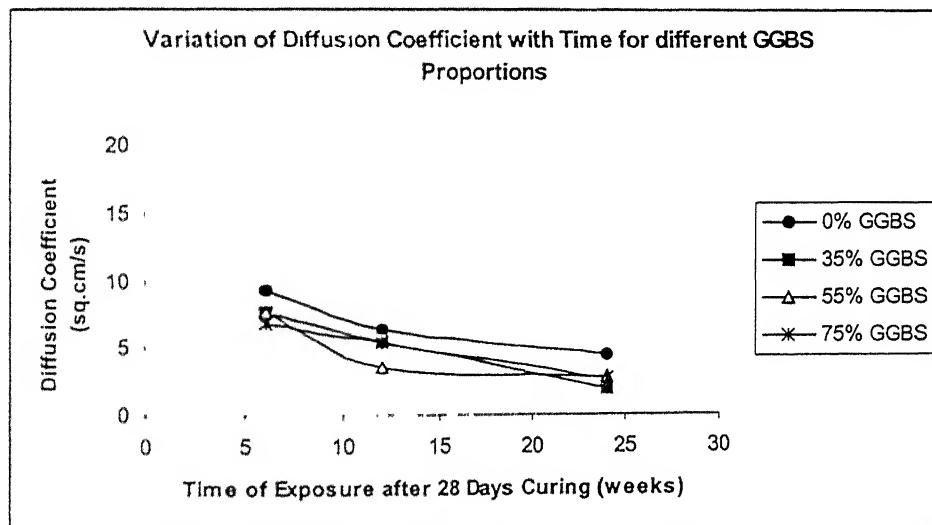


Figure 5.46: Apparent Diffusion Coefficient, (in $10^{-8} \cdot \text{cm}^2/\text{s}$), of concrete with W/B ratio 0.4, exposed to continuous immersion in 3.5 % NaCl solution.

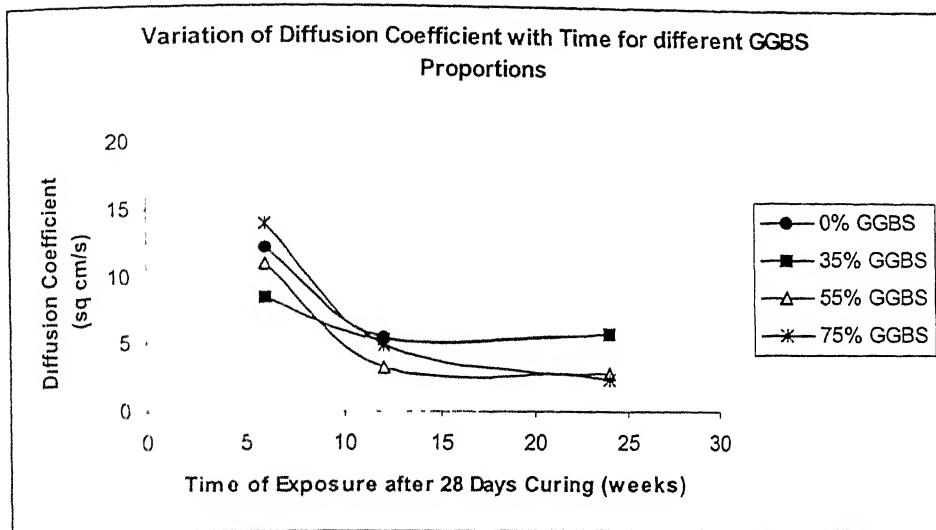


Fig. 5.47: Apparent diffusion coefficient, (in $10^{-8} \cdot \text{cm}^2/\text{s}$), of concrete with W/B ratio 0.5, exposed to continuous immersion in 3.5 % NaCl solution.

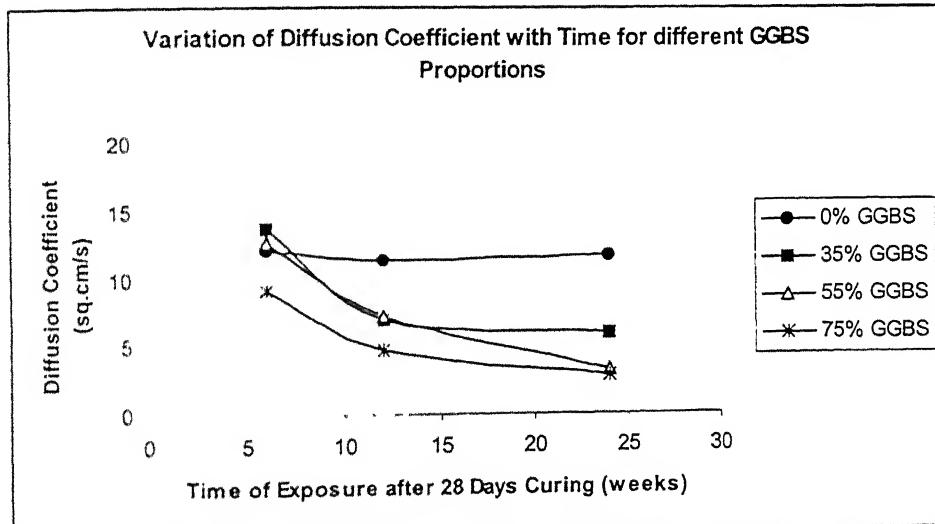


Figure 5.48: Apparent diffusion coefficient, (in $10^{-8} \cdot \text{cm}^2/\text{s}$), of concrete with W/B ratio 0.6, exposed to continuous immersion in 3.5 % NaCl solution.

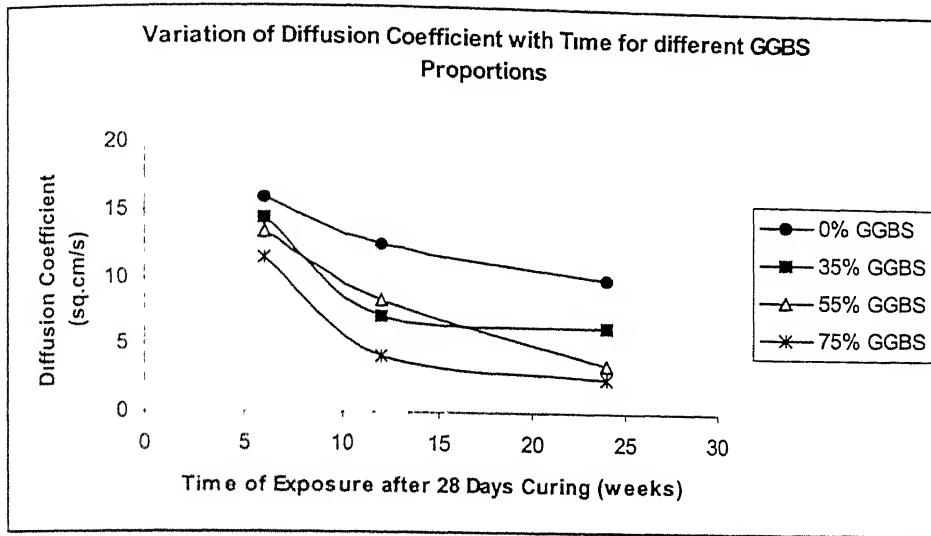


Fig. 5.49: Apparent diffusion coefficient, (in $10^{-8} \text{ cm}^2/\text{s}$), of concrete with W/B ratio 0.6, exposed to alternate wetting and drying cycles in 3.5 % NaCl solution.

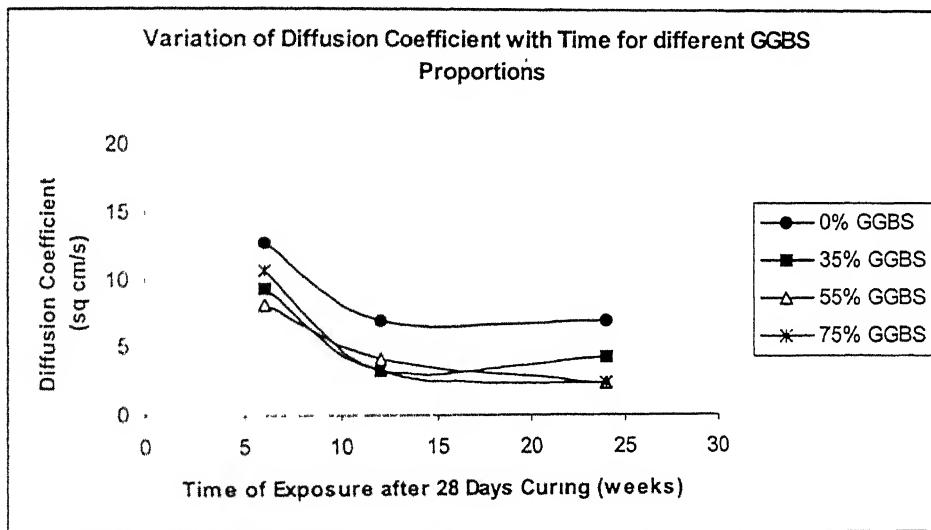


Figure 5.50: Apparent diffusion coefficient, (in $10^{-8} \text{ cm}^2/\text{s}$), of concrete with W/B ratio 0.4, exposed to continuous submersion in 7.0 % NaCl solution.

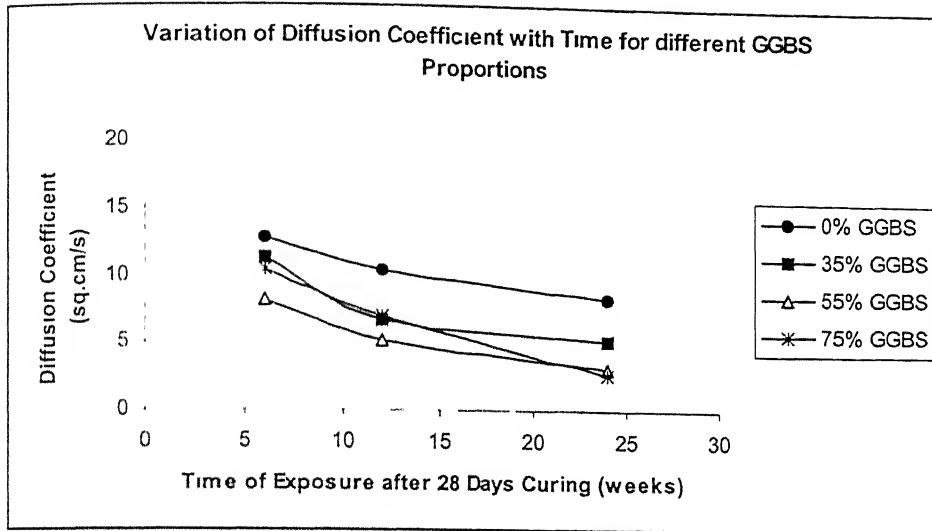


Figure 5.51: Apparent diffusion coefficient, (in $10^{-8} \text{.cm}^2/\text{s}$), of concrete with W/B ratio 0.5 exposed to continuous submersion in 7.0 % NaCl solution.

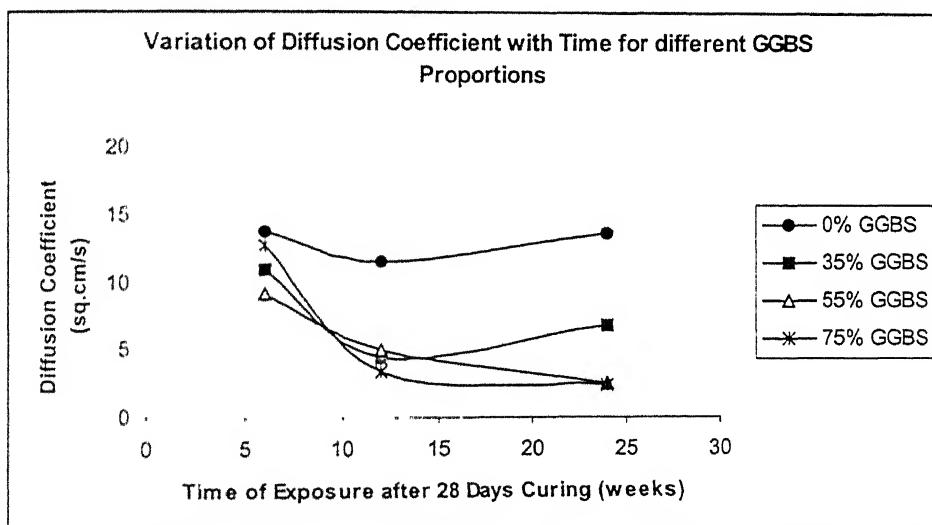


Figure 5.52: Apparent diffusion coefficient, (in $10^{-8} \text{.cm}^2/\text{s}$), of concrete with W/B ratio 0.6 exposed to continuous submersion in 7.0 % NaCl solution.

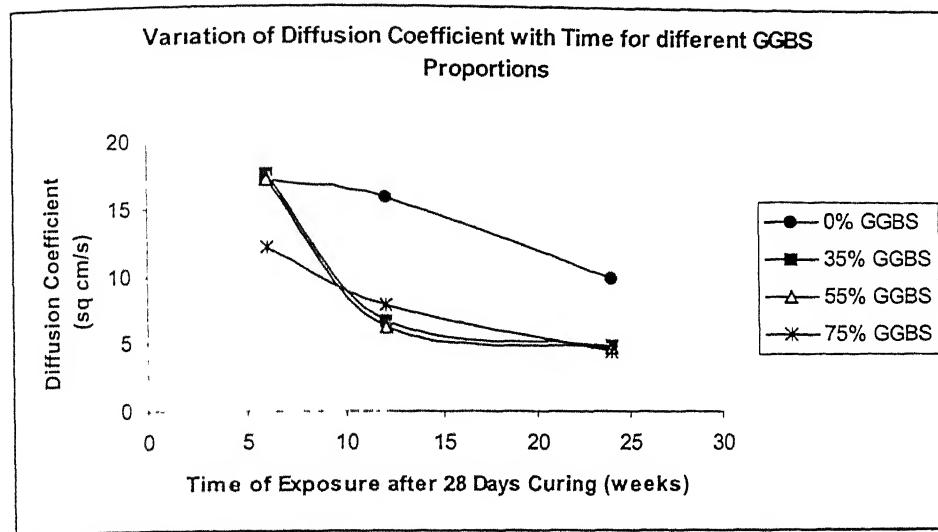


Figure 5.53: Apparent diffusion coefficient, (in $10^{-8} \cdot \text{cm}^2/\text{s}$), of concrete with W/B ratio 0.6, exposed to alternate wetting and drying cycles in 7.0 % NaCl solution.

Chapter 6

CONCLUDING REMARKS

6.1 General

This study focused on effects of utilization of GGBS (in varying amounts) on the properties of concrete, in terms of its strength development and resistance to chloride penetration. The experimental program and results have been discussed in the earlier chapters. The following conclusions can be drawn within the limitations of the work carried out in this study.

6.2 Properties of fresh concrete

It was observed during concrete mixing and casting that slag concretes provide better cohesion and the paste is more gel like than OPC concretes. Contradictory results have been reported in literature about the workability of slag concretes compared to OPC concretes, but in this study it was found that incorporation of slag does not adversely affect workability of fresh concrete. The compaction factor of the fresh concrete of all the mixes (had same water and aggregate content) was observed to range between 0.845 ± 0.015 .

6.3 Strength development in concrete

The initial strength development is slow in concrete containing GGBS but if curing is continued then the strength at 28 days becomes comparable to that of OPC concrete for concretes upto 55% slag replacement. The slag concretes gain considerable strength after 28

days also and 35% replacement of OPC by GGBS gave higher compressive strength at 56 days and onward. 35% 45% replacement level is observed to be optimum from strength point of view, after which the compressive strength again decreases.

6.4 Resistance to chloride penetration

Use of GGBS greatly enhances resistance to chloride penetration in concrete, and the resistance to chloride penetration increases with increase in proportion of GGBS up to 75% replacement level, studied in this work. It should be noted that this improvement in resistance to chloride penetration (pore refinement) is obtained, even if compressive strength is adversely affected (at larger levels of replacement)

The apparent diffusion coefficient of GGBS containing concrete decreases significantly with time. Though at the exposure duration of 6 weeks 'D' of GGBS containing concretes is only slightly less compared to OPC concrete, however it decreases dramatically with time. At the age of 24 weeks the 'D' of 55% and 75% replacement concretes are only 50%, 33% and, 25% of the 'D' of OPC control concrete for W/B 0.4, 0.5 and, 0.6 respectively. Also, though the diffusion coefficient of OPC concretes is not expected to decrease further after 24 weeks, but that of higher GGBS concretes tends to continue to decrease further.

Further, to actually reach the equilibrium level the surface concentration takes considerable time and it increases through out the duration of the test (24 weeks). With increase in exposure concentration of chloride ions the equilibrium surface concentration ' C_s ' increases proportionately, but there is only slight increase in the diffusion coefficient.

6.5 Quality control in concretes containing slag

Since concretes containing slag continues to gain strength till a longer period, in cases when GGBS is being used, 91-day strength is more representative of concrete quality than the 28-day strength, which is the basis for most of the quality control measures generally used in concrete construction.

Also, though compressive strength is a good indication of durability potential of OPC concretes, the same is not true for concrete containing GGBS, and permeability may need to be treated as a completely independent parameter in these concretes.

6.6 Scope for future work

The mechanical and durability properties of GGBS concretes are very sensitive to curing condition, i.e. temperature and humidity. This study has been carried out without making specific efforts to maintain these quantities at a predetermined level. Now, given the fact that GGBS concrete is more sensitive to curing conditions, further study in this respect needs to be carried out. Further studies need also to be carried out by using GGBS from different sources.

Though a limited number of tests were carried out to determine the 'soluble' chloride and compare these values to the 'total' chloride, the results were unfortunately inconclusive. Given the importance of this parameter w.r.t the corrosion of reinforcing bars, it is suggested that some more studies in this direction are carried out.

REFERENCES:

ACI Committee 233, 2000, "Guidelines for Use of Ground Granulated Blast-Furnace Slag in Concrete", ACI Manual, Part-I.

Almussalam, A.A., Maslehuddin, M., Abdul-Waris, M., Dakhil, F.H. & Al-Amoudi, O.S B., 1999, "Plastic Shrinkage Cracking of Blended Cement Concretes in Hot Environments", Magazine of Concrete Research, Vol.51, No.4, pp.241-246.

Andrade, C., 1993, "Calculation of Chloride Diffusion Coefficient in Concrete from Ionic Migration Measurement", Cement and Concrete Research, Vol.23, No.3, pp.724-742.

Andrade, C., Castellote, M., Cervigon, D. & Alonso, C., 1996, "Influence of External Concentration and Testing time on Chloride Diffusion Coefficient Values of Steady and Non-Steady State Migration Experiments", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.76-83.

Andrade, C., Sanjuan, M.A., Recuero, A. & Rio, O., 1994, "Calculation of Chloride Diffusivity in Concrete from Migration Experiments in Non-Steady State Conditions", Cement and Concrete Research, Vol.24, No.7, pp.1214-1221.

Bentz, E.C., Thomas, M.D.A. & Evans, C.M., 1996, "Chloride Diffusion Modeling for Marine Exposed Concrets" Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.136-145.

Bijen, J., 2000, "Slag Cement for Durable Concrete", Workshop on Slag Based Composite Cement, Patna, Organized by ACC.

Carpinteri, A., Ferro, G., and Monetto, I., 1999, "Scale Effect in Uniaxially Compressed Concrete Specimens", Magazine of Concrete Research, Vol.51, No.3, pp 217-225

Castellote, M., Andrade, C. & Alonso, C., 1999, "Chloride-Binding Isotherm in Concrete Submitted to Non-Steady State Migration Experiments", Cement and Concrete Research, Vol.29, pp.1799-1806.

Chern, J.C. & Chan, Y.W., 1989, "Effect of Temperature and Humidity Conditions on the Strength of Blast Furnace Slag Concrete", ACI, SP-114, pp.1377-1397.

Climent, M.A., Vigueira, E., Vera, G. de & Atalaya, M.M.L., 1999, "Analysis of Acid- Soluble Chloride in Cement, Mortar, and Concrete by Potentiometric Titration Without Filtration Steps", Concrete And Cement Research, Vol.29, No.6, pp.893-898.

Constantinou, A.G. & Scrivener, K.L., 1995, "Microstructural Examination of the Development of Corrosion in Reinforced Concrete", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.134-142.

Cook, D.J., Hinczak, I., Jedy, M. & Cao, H.T., 1989, "The Behaviour of Slag Cement Concretes in Marine Environment – Chloride Ion Penetration", ACI, SP-114, pp.1467-1483.

Cranck, J., 1975, "The Mathematics of Diffusion", Ed. Oxford University Press New York.

Deeter, M.H., Short, N.R., Page, C.L. & Higgins, D.D., 1989, "Chloride Ion Penetration into Blended Cement Pastes and Concretes", ACI, SP-114, pp.1399-1411.

Detwiler, R.J., Kjellson, K.O. & Gjorv, O.E., 1991, "Resistance to Chloride Intrusion of Concrete Cured at Different Temperatures", ACI Material Journal, Vol.88, No.1, pp.19-24.

Feldman, R.F., Chan, G.W., Brousseau, R.J. & Tumidajski, P.J., 1994, "Investigation of Rapid Chloride Permeability Test", ACI Material Journal, Vol.91, No.2, pp.246-255.

Frearson, J.P.H & Higgins, D.D., 1995, "Effect of Test Procedures on the Assessment of the Sulfate Resistance of Slag Cements", ACI, SP-153, Vol.2, pp.975-993.

Japan Society of Civil Engineering, 1986, "Guidelines for Construction of Concrete Using GGBS", Concrete Library, Vol.86.

Gulikers, J. & Schlangen, E., 1996, "Numerical Analysis of Galvanic Interaction in Reinforcement Corrosion", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.3-12.

Higgins, D.D. & Connell, M.D., 1995, "Effectiveness of Granulated Blast Furnace Slag in Preventing Alkali-Silica Reactions", ACI, SP-153, Vol.2, pp.1017-1030.

Hobbs, D.W., 1996, "Chloride Ingress and Chloride-Induced Corrosion in Reinforced Concrete Members", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.124-135

Hogan, F.J., and Meusel, J.W., 1981 "Evaluation for Durability and Strength Development of a Ground Granulated Blast-Furnace Slag Cement", Cement, Concrete, and Aggregates, V.3, No.4, pp.40-52.

Hogan, F.J., 1983, "The Effect of Blast Furnace Slag on Alkali Aggregate Reactivity: A Literature Review", Cement Concrete and Aggregate, Vol.7, no 2, pp.100-107.

Hooton, R.D., "The Reactivity and Hydration Products of Blast-Furnace Slag", Supplementary Cementing Material for Concrete, Edited by Malhotra, V.M., Chater.4, pp.247-288.

Hooton, R.D. & Emery, J.J., 1983 "Glass Content Determination and Strength Development Prediction for Vitrified Blast Furnace Slag", ACI, SP-79, Vol.2, pp.943-962.

Lim, S.N., and Wee, T.H., 2000, "Autogenous Shrinkage of Ground-Granulated Blast-Furnace Slag Concrete", ACI Material Journal, Vol.97, No.5, pp.587-592.

Malhotra, V.M., "Properties of Fresh and Hardened Concrete Incorporating Ground, Granulated, Blast-Furnace Slag", Supplementary Cementing Material for Concrete, Edited by Malhotra, V.M., Chater.5, pp.291-333.

Manmohan, D., and Mehata, P.K., 1981, "Influence of Pozzolanic Slag and Chemical Admixtures on Pore Size Distribution and Permeability of Hydrated Cement Pastes", Cement, Concrete, and Aggregate, V.3, No.1, pp.63-67.

Mather, Bryant, 1957, "Laboratory Tests of Portland Blast-Furnace Slag Cement", ACI journal, V.54, No.3, pp.205-232.

Meusel, J.W. & Rose, J.H., 1983, "Production of Granulated Blast Furnace Slag at Sparrows Point, and the Workability and Strength Potential of Concrete Incorporating the Slag", ACI, SP-79, Vol.2, pp.867-890.

Miura, T., and Iwaki, I., 1998, "Effect of Curing Methods in Cold Regions on Strength of Concrete Incorporating Ground Granulated Blast Furnace Slag", Fourth CANMET/ACI/JCI International Symposium, ACI, SP.179, pp.815-829.

Morsy, M.S., 1999, "Effect of Temperature on Electrical Conductivity of Blended Cement Pastes", Concrete And Cement Research, Vol.29, No.4, pp.603-606.

Murata, J., Kawasaki, M., Sakai, T. & Kawai, T., 1983, "Resistance to Freezing and Thawing of Concrete Using Ground Blast-Furnace Slag", ACI, SP-79, Vol.2, pp.999-1011.

Nakamoto, J. & Togawa, K., 1995, "A Study of Strength Development and Carbonation of Concrete Incorporating High Volume Blast Furnace Slag", ACI, SP-153, Vol.2, pp.1121-1139.

Nakamoto, J & Togawa, K., Miyagawa, T., Fuji, M., and Nagaoka, S., 1998, "Freezing and Thawing Resistance of High Slag Content Concrete", Fourth CANMET/ACI/JCI International Symposium, ACI, SP.179, pp.1059-1072.

Nishibayashi, S., Kuroda, T., and Okawa, Y., "Promising Approach to Prevent Alkali Aggregate reaction in Concrete – Effect of Blast Furnace Slag", Proceedings Second CANMET/ACI International Symposium, USA, ACI, SP-154, pp.229-244.

Osborne, G.J., 1989, "Carbonation and Permeability of Blast Furnace Slag Concrete from Field Structures", ACI, SP-114, pp.1209-1237.

Osborne, G.J., 1992, "The performance of Portland and Blast Furnace Slag Cement Concretes in Marine Environment", ACI, SP-132, Vol.2, pp.1302-1323.

Pigeon, M. & Regourd, M., "Freezing and Thawing Durability of Three Cements with Various Granulated Blast Furnace Slag Contents", ACI, SP-79, Vol.2, pp.979-998.

Polder, R.B., 1996, "Laboratory Testing of Five Concrete Types for Durability in a Marine Environment", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.115-123.

Prasad, G.V.K. & Babu, L.V.R.L., 1999, "Use of Ground Granulated Blast Furnace Slag (GGBS) for Durable Concrete", Proceedings of Fifth International Conference on Concrete Technology for Developing Countries, Vol.1, pp.II.12-II.22.

Rajkumar, C., 1998, "Properties of Cement and Concrete Containing Granulated Blast Furnace Slag", Proceedings of National Seminar on Performance Enhancement of Cements and Concretes by Use of Fly Ash, Slag, Silica Fume and Chemical Admixtures, New Delhi, pp.II.165-178.

Rasheeduzzafar, Hussain, S.E. & Al-Saadoun, S.S., 1992, "Effect of Tricalcium Aluminate Content of Cement on Chloride Binding and Corrosion of Reinforcing Steel in Concrete", ACI Material Journal, Vol.89, No.1, pp.3-12.

Roy, D.M., 1989, "Hydration, Microstructure, and Chloride Diffusion of Slag-Cement Pastes and Mortars", ACI, SP-114, pp.1265-1281.

Roy, D.M. & Jiang, W., 1995, "Concrete Chemical Degradation Ancient Analogues and Modern Evaluation", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.14-21.

Sanjayan, J.G., and Sioulas, B., 2000, "Strength of Slag-Cement Concrete Cured in Place and in Other Conditions", ACI Material Journal, Vol.97, No.5, pp.603-611.

Shane, J.D., Hwang, J.H., Sohn, D., Mason, T.O., Jennings, H.M. & Garboczi, E.J., 1995, "Recent Developments in Measurement of Transport Properties in Cement-Based Materials", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.413-423.

Sharma, K.M. & Mohan, K., 1998, "Characterisation and Utilisation of Indian Slag", Proceedings of National Seminar on Performance Enhancement of Cements and Concretes by Use of Fly Ash, Slag, Silica Fume and Chemical Admixtures, New Delhi, pp.II.132-140.

Streicher, P.E. & Alexander, M.G., 1995, "Diffusibility Changes due to Presence of Chloride Ions", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.50-57.

Swamy, R.N., 1999, "Role of Slag in Development of Durable, Sustainable High Strength Concrete", Proceedings of the International Symposium on Concrete Technology for Sustainable Development in the Twenty-First Century, Hyderabad, India, pp.186-221.

Swamy, R.N. & Boukini, A., 1990, "Some Properties of Slag Concrete as Influenced by Mix Proportioning and Curing", ACI Material Journal, V.87, pp.210-220.

Swamy, R.N. & Laiw, J.C., 1995, "Effectiveness of Supplementary Cementing Materials in Controlling Chloride Penetration into Concrete", ACI, SP-153, Vol.2, pp.657-674.

Tanaka, H., Totani, Y. & Saito, Y., 1983, "Structure of Hydrated Glassy Blast Furnace Slag in Concrete", ACI, SP-79, Vol.2, pp.963-977.

Tang, L. & Nilsson, L.O., 1992, "Rapid Determination of Chloride Diffusivity of Concrete by Applying an Electric Field", ACI Material Journal, Vol.89, No.1, pp.49-53.

Tang, L. & Nilsson, L.O., 1995, "Accelerated Test for Chloride Diffusivity and Their Application in Prediction of Chloride Penetration", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp 387-396.

Tang, L. & Sandberg, P., 1996, "Chloride Penetration in Concrete Exposed under Different Conditions", Proceedings of the Seventh International Conference on Durability of Building Materials and Components, 7DBMC, Sweden, Vol.1, pp.453-461.

Thomas, M.D.A. & Bamforth, P.B., 1999, "Modeling Chloride Diffusion in Concrete: Effect of Fly Ash and Slag", Concrete and Cement Research, Vol.29, pp.487-495.

Tomisawa, T. & Fuji, M., 1995, "Effect of High Fineness and Large Amounts of Ground Granulated Blast Furnace Slag on Properties and Microstructure of Slag Cement", ACI, SP-153, Vol.2, pp.951-973.

Virtanen, J., 1983, "Freeze-Thaw Resistance of Concrete Containing Blast-Furnace Slag, Fly-Ash or Silica Fume", ACI, SP-79, Vol.2, pp.923-942.

Walton, J.C. et al, 1995, "Role of Carbonation in Long Term Performance of Cementitious Wastes", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.315-322

Wang, T., Nishibayashi, S., Nakano, K. & Bian, Q., 1995, "Effect of Blast Furnace Slag in Reducing Expansion due to Alkali-Silica Reaction in Concrete", ACI, SP-153, Vol.2, pp.1069-1086.

Wason, R.C., Mehta, S.K. & Kumar, S., 1999, "Durability Studies on Concrete Containing Portland Slag Cement", Proceedings of Fifth International Conference on Concrete Technology for Developing Countries, Vol.1, pp.IV.42-IV.52.

Wimpenny, D.E., Ellis, C., Reeves, C.M. & Higgins, D.D., 1989, "The Development of Strength and Elastic Properties in Slag Cement Concretes Under Low Temperature Curing Conditions", ACI, SP-114, pp.1283-1306.

Xi, Y., 1995, "Mathematical Modeling of Chloride Diffusion in Concrete", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp 397-404.

Xu, A. & Chandra, S., 1994, "A Discussion of the Paper – Calculation of Chloride Diffusion Coefficient in Concrete from Ionic Migration Measurement – by C. Andrade", Cement and Concrete Research, Vol.24, No.2, pp.375-379.

Yamada, Y., Oshiro, T., and Masuda, Y., 1998, "Study of Penetrating Process of Chloride Ions in Concrete", Fourth CANMET/ACI/JCI International Symposium, ACI, SP.179, pp.331-345.

REFERENCES:

Standards

IS 455 (1967) "Specifications for Portland Blast-Furnace slag cement".
IS. 516 (1959) "Method of Tests for Strength of Concrete".
BS 6699 (1992) "Specifications for Ground Granulated Blast-furnace Slag for Use with Portland Cement".
ASTM. C-989 (1995) "Ground Granulated Blast-furnace Slag for Use in Concrete and Mortars"

Papers and Proceedings

ACI Committee 233, 2000, "Guidelines for Use of Ground Granulated Blast-Furnace Slag in Concrete", ACI Manual, Part-I.

Almussalam, A A., Maslehuddin, M., Abdul-Waris, M., Dakhil, F.H. & Al-Amoudi, O.S.B , 1999, "Plastic Shrinkage Cracking of Blended Cement Concretes in Hot Environments", Magazine of Concrete Research, Vol.51, No.4, pp.241-246

Andrade, C., 1993, "Calculation of Chloride Diffusion Coefficient in Concrete from Ionic Migration Measurement", Cement and Concrete Research, Vol.23, No.3, pp 724-742.

Andrade, C., Castellote, M , Cervigon, D & Alonso, C., 1996, "Influence of External Concentration and Testing time on Chloride Diffusion Coefficient Values of Steady and Non-Steady State Migration Experiments", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.76-83.

Andrade, C., Sanjuan, M A., Recuero, A. & Rio, O , 1994, "Calculation of Chloride Diffusivity in Concrete from Migration Experiments in Non-Steady State Conditions", Cement and Concrete Research, Vol.24, No.7, pp.1214-1221.

Bentz, E.C., Thomas, M.D.A. & Evans, C M., 1996, "Chloride Diffusion Modeling for Marine Exposed Concretes" Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No 183, pp.136-145.

Bijen, J., 2000, "Slag Cement for Durable Concrete", Workshop on Slag Based Composite Cement, Patna, Organized by ACC.

Carpinteri, A , Ferro, G., and Monetto, I., 1999, "Scale Effect in Uniaxially Compressed Concrete Specimens", Magazine of Concrete Research, Vol.51, No.3, pp.217-225.

Castellote, M., Andrade, C. & Alonso, C., 1999, "Chloride-Binding Isotherm in Concrete Submitted to Non-Steady State Migration Experiments", Cement and Concrete Research, Vol.29, pp.1799-1806.

Chern, J.C. & Chan, Y.W., 1989, "Effect of Temperature and Humidity Conditions on the Strength of Blast Furnace Slag Concrete", ACI, SP-114, pp.1377-1397.

Climent, M.A., Vigueira, E., Vera, G. de & Atalaya, M M.L., 1999, "Analysis of Acid- Soluble Chloride in Cement, Mortar, and Concrete by Potentiometric Titration Without Filtration Steps", Concrete And Cement Research, Vol.29, No.6, pp.893-898.

Constantinou, A.G & Scrivener, K.L., 1995, "Microstructural Examination of the Development of Corrosion in Reinforced Concrete", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.134-142.

Cook, D J , Hinczak, I , Jedy, M & Cao, H.T , 1989, "The Behaviour of Slag Cement Concretes in Marine Environment – Chloride Ion Penetration", ACI, SP-114, pp.1467-1483.

Crank, J., 1975, "The Mathematics of Diffusion", Ed. Oxford University, Press New York.

Deeter, M.H., Short, N R., Page, C.L. & Higgins, D.D., 1989, "Chloride Ion Penetration into Blended Cement Pastes and Concretes", ACI, SP-114, pp 1399-1411.

Detwiler, R.J., Kjellson, K.O. & Gjorv, O E , 1991, "Resistance to Chloride Intrusion of Concrete Cured at Different Temperatures", ACI Material Journal, Vol 88, No.1, pp 19-24

Feldman, R.F., Chan, G.W , Brousseau, R.J. & Tumidajski, P.J , 1994, "Investigation of Rapid Chloride Permeability Test", ACI Material Journal, Vol 91, No.2, pp 246-255.

Frearson, J P.H & Higgins, D D., 1995, "Effect of Test Procedures on the Assessment of the Sulfate Resistance of Slag Cements", ACI, SP-153, Vol.2, pp 975-993

Japan Society of Civil Engineering, 1986, "Guidelines for Construction of Concrete Using GGBS", Concrete Library, Vol.86.

Gulikers, J. & Schlangen, E., 1996, "Numerical Analysis of Galvanic Interaction in Reinforcement Corrosion", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No 183, pp 3-12.

Higgins, D D. & Connell, M.D., 1995, "Effectiveness of Granulated Blast Furnace Slag in Preventing Alkali-Silica Reactions", ACI, SP-153, Vol 2, pp 1017-1030.

Hobbs, D W., 1996, "Chloride Ingress and Chloride-Induced Corrosion in Reinforced Concrete Members", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No 183, pp.124-135

Hogan, F.J., and Meusel, J.W., 1981 "Evaluation for Durability and Strength Development of a Ground Granulated Blast-Furnace Slag Cement", Cement, Concrete, and Aggregates, V.3, No.4, pp 40-52.

Hogan, F J., 1983, "The Effect of Blast Furnace Slag on Alkali Aggregate Reactivity. A Literature Review", Cement Concrete and Aggregate, Vol 7, no.2, pp.100-107.

Hooton, R.D., "The Reactivity and Hydration Products of Blast-Furnace Slag", Supplementary Cementing Material for Concrete, Edited by Malhotra, V.M., Chater 4, pp.247-288.

Hooton, R.D. & Emery, J.J., 1983 "Glass Content Determination and Strength Development Prediction for Vitrified Blast Furnace Slag", ACI, SP-79, Vol.2, pp.943-962

Lim, S.N., and Wee, T.H., 2000, "Autogenous Shrinkage of Ground-Granulated Blast-Furnace Slag Concrete", ACI Material Journal, Vol.97, No.5, pp.587-592.

Malhotra, V.M., 1980, "Properties of Fresh and Hardened Concrete Incorporating Ground, Granulated, Blast-Furnace Slag", Supplementary Cementing Material for Concrete, Edited by Malhotra, V.M., Chater.5, pp.291-333.

Manmohan, D., and Mehata, P.K., 1981, "Influence of Pozzolanic Slag and Chemical Admixtures on Pore Size Distribution and Permeability of Hydrated Cement Pastes", Cement, Concrete, and Aggregate, V.3, No.1, pp.63-67.

Mather, Bryant, 1957, "Laboratory Tests of Portland Blast-Furnace Slag Cement", ACI journal, V 54, No.3, pp 205-232.

Meusel, J W & Rose, J H., 1983, "Production of Granulated Blast Furnace Slag at Sparrows Point, and the Workability and Strength Potential of Concrete Incorporating the Slag", ACI, SP-79, Vol 2, pp.867-890.

Miura, T , and Iwaki, I., 1998, "Effect of Curing Methods in Cold Regions on Strength of Concrete Incorporating Ground Granulated Blast Furnace Slag", Fourth CANMET/ACI/JCI International Symposium, ACI, SP 179, pp.815-829

Morsy, M S , 1999, "Effect of Temperature on Electrical Conductivity of Blended Cement Pastes", Concrete And Cement Research, Vol.29, No 4, pp.603-606.

Murata, J., Kawasaki, M , Sakai, T & Kawai, T , 1983, "Resistance to Freezing and Thawing of Concrete Using Ground Blast-Furnace Slag", ACI, SP-79, Vol.2, pp.999-1011.

Nakamoto, J & Togawa, K., 1995, "A Study of Strength Development and Carbonation of Concrete Incorporating High Volume Blast Furnace Slag", ACI, SP-153, Vol 2, pp.1121-1139

Nakamoto, J. & Togawa, K., Miyagawa, T., Fuji, M , and Nagaoka, S., 1998, "Freezing and Thawing Resistance of High Slag Content Concrete", Fourth CANMET/ACI/JCI International Symposium, ACI, SP 179, pp.1059-1072

Nishibayashi, S., Kuroda, T., and Okawa, Y., "Promising Approach to Prevent Alkali Aggregate reaction in Concrete - Effect of Blast Furnace Slag", Proceedings Second CANMET/ACI International Symposium, USA, ACI, SP-154, pp.229-244.

Osborne, G J., 1989, "Carbonation and Permeability of Blast Furnace Slag Concrete from Field Structures", ACI, SP-114, pp.1209-1237.

Osborne, G.J., 1992, "The performance of Portland and Blast Furnace Slag Cement Concretes in Marine Environment", ACI, SP-132, Vol.2, pp.1302-1323.

Pigeon, M. & Regourd, M , 1983, "Freezing and Thawing Durability of Three Cements with Various Granulated Blast Furnace Slag Contents", ACI, SP-79, Vol 2, pp.979-998.

Polder, R.B , 1996, "Laboratory Testing of Five Concrete Types for Durability in a Marine Environment", Corrosion of Reinforcement in Concrete Construction, Edited by Page, Bamforth, and Figg, SCI, Special Publication No.183, pp.115-123

Prasad, G.V.K. & Babu, L.V.R.L., 1999, "Use of Ground Granulated Blast Furnace Slag (GGBS) for Durable Concrete", Proceedings of Fifth International Conference on Concrete Technology for Developing Countries, Vol.1, pp.II.12-II.22.

Rajkumar, C., 1998, "Properties of Cement and Concrete Containing Granulated Blast Furnace Slag", Proceedings of National Seminar on Performance Enhancement of Cements and Concretes by Use of Fly Ash, Slag, Silica Fume and Chemical Admixtures, New Delhi, pp II.165-178.

Rasheeduzzafar, Hussain, S.E. & Al-Saadoun, S.S., 1992, "Effect of Tricalcium Aluminate Content of Cement on Chloride Binding and Corrosion of Reinforcing Steel in Concrete", ACI Material Journal, Vol.89, No.1, pp.3-12.

Roy, D.M., 1989, "Hydration, Microstructure, and Chloride Diffusion of Slag-Cement Pastes and Mortars", ACI, SP-114, pp.1265-1281.

Roy, D.M. & Jiang, W., 1995, "Concrete Chemical Degradation: Ancient Analogues and Modern Evaluation", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.14-21.

Sanjayan, J G., and Sioulas, B., 2000, "Strength of Slag-Cement Concrete Cured in Place and in Other Conditions", ACI Material Journal, Vol 97, No 5, pp 603-611.

Shane, J.D , Hwang, J.H , Sohn, D , Mason, T.O , Jennings, H.M. & Garboczi, E J., 1995, "Recent Developments in Measurement of Transport Properties in Cement-Based Materials", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp 413-423

Sharma, K M. & Mohan, K , 1998, "Characterisation and Utilisation of Indian Slag", Proceedings of National Seminar on Performance Enhancement of Cements and Concretes by Use of Fly Ash, Slag, Silica Fume and Chemical Admixtures, New Delhi, pp.II.132-140.

Streicher, P.E. & Alexander, M.G., 1995, "Diffusibility Changes due to Presence of Chloride Ions", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.50-57.

Swamy, R.N., 1999, "Role of Slag in Development of Durable, Sustainable High Strength Concrete", Proceedings of the International Symposium on Concrete Technology for Sustainable Development in the Twenty-First Century, Hyderabad, India, pp.186-221.

Swamy, R.N. & Boukini, A., 1990, "Some Engineering Properties of Slag Concrete as Influenced by Mix Proportioning and Curing", ACI Material Journal, V 87, pp 210-220

Swamy, R N & Laiw, J.C., 1995, "Effectiveness of Supplementary Cementing Materials in Controlling Chloride Penetration into Concrete", ACI, SP-153, Vol.2, pp.657-674.

Tanaka, H., Totani, Y & Saito, Y , 1983, "Structure of Hydrated Glassy Blast Furnace Slag in Concrete", ACI, SP-79, Vol.2, pp.963-977.

Tang, L. & Nilson, L.O., 1992, "Rapid Determination of Chloride Diffusivity of Concrete by Applying an Electric Field", ACI Material Journal, Vol.89, No.1, pp.49-53

Tang, L. & Nilsson, L.O , 1995, "Accelerated Test for Chloride Diffusivity and Their Application in Prediction of Chloride Penetration", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.387-396

Tang, L. & Sandberg, P., 1996, "Chloride Penetration in Concrete Exposed under Different Conditions", Proceedings of the Seventh International Conference on Durability of Building Materials and Components, 7DBMC, Sweden, Vol.1, pp.453-461.

Thomas, M.D A. & Bamforth, P B., 1999, "Modeling Chloride Diffusion in Concrete: Effect of Fly Ash and Slag ", Concrete and Cement Research, Vol.29, pp 487-495.

Tomisawa, T. & Fuji, M., 1995, "Effect of High Fineness and Large Amounts of Ground Granulated Blast Furnace Slag on Properties and Microstructure of Slag Cement", ACI, SP-153, Vol.2, pp 951-973.

Virtanen, J., 1983, "Freeze-Thaw Resistance of Concrete Containing Blast-Furnace Slag, Fly-Ash or Silica Fume", ACI, SP-79, Vol.2, pp.923-942.

Walton, J.C. et al, 1995, "Role of Carbonation in Long Term Performance of Cementitious Wasteforms", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.315-322.

Wang, T., Nishibayashi, S., Nakano, K. & Bian, Q., 1995, "Effect of Blast Furnace Slag in Reducing Expansion due to Alkali-Silica Reaction in Concrete", ACI, SP-153, Vol.2, pp.1069-1086.

Wason, R.C , Mehta, S K. & Kumar, S , 1999, "Durability Studies on Concrete Containing Portland Slag Cement", Proceedings of Fifth International Conference on Concrete Technology for Developing Countries, Vol 1, pp IV.42-IV 52

Wimpenny, D.E., Ellis, C , Reeves, C M & Higgins, D.D., 1989, "The Development of Strength and Elastic Properties in Slag Cement Concretes Under Low Temperature Curing Conditions", ACI, SP-114, pp.1283-1306

Xi, Y , 1995, "Mathematical Modeling of Chloride Diffusion in Concrete", Mechanism of Chemical Degradation of Cement-Based Systems, Proceedings of the Material Research Society's Symposium, Boston, USA, pp.397-404

Xu, A. & Chandra, S., 1994, "A Discussion of the Paper – Calculation of Chloride Diffusion Coefficient in Concrete from Ionic Migration Measurement – by C Andrade", Cement and Concrete Research, Vol.24, No.2, pp.375-379.

Yamada, Y., Oshiro, T , and Masuda, Y., 1998, "Study of Penetrating Process of Chloride Ions in Concrete", Fourth CANMET/ACI/JCI International Symposium, ACI, SP 179, pp 331-345.

Appendix - 1

A1.1 Basic Diffusion Equation

Fick's first law states, "in an isotropic medium the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section" i.e.

$$J = -D \frac{\partial C}{\partial x} \quad (a.1.1)$$

Where,

J = flux of diffusing substance

C = concentration of diffusing substance

x = space co-ordinate normal to the section

and, D = diffusion coefficient

Now from basic calculus and theory of continuity we get the fundamental differential equation of diffusion in an isotropic medium and that is given by

$$\frac{\partial C}{\partial t} + \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} = 0 \quad (a.1.2)$$

Now, if D is constant with respect to space co-ordinates and the diffusion is one dimensional, i.e. if there is a gradient of concentration only along the x -axis, then equation (a.1.2) becomes:

$$\begin{aligned} \frac{\partial C}{\partial t} &= -\frac{\partial J_x}{\partial x} \\ \Rightarrow \frac{\partial C}{\partial t} &= -D \frac{\partial^2 C}{\partial x^2} \end{aligned} \quad (a.1.3)$$

Equation (a.1.3) is usually referred to as Fick's second law of diffusion. This is the fundamental equation, which is often used for mathematical modeling of diffusion process in concrete.

A1.2 Solution of Diffusion equation

If the diffusion coefficient is constant or an integrable function of time (t), the above differential equation can be solved for a given set of initial and boundary conditions. In a simplified case for a concrete wall submerged in chloride solution, in which we assume that concentration of chloride in a thin layer at the surface reaches at equilibrium and remains constant soon after the exposure, these initial and boundary conditions can be taken as:

Boundary condition,

$$C = C_s, x = 0, t > 0$$

Initial condition,

$$C = 0, x > 0, t = 0$$

And, infinite point condition is,

$$C = 0, x \rightarrow \infty, t = t_M$$

Where,

C_s is the pseudo equilibrium concentration at $x=0$, i.e on the exposure surface, at all time.

And, t_M is a large infinite number

Using these initial and boundary conditions, and assuming that no chloride, which enters the concrete, is adsorbed or bound by the concrete matrix and is free for further diffusion or the chloride binding isotherm is linear and diffusion coefficient is constant with respect to time and space, we get the solution of equation (a.1.3) as:

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (\text{a.14})$$

Where, $\operatorname{erf}(z)$ is the standard error function, given as.

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$

It is a standard mathematical function and extensive tables of it are available.

If there is some chloride present in the concrete from its ingredients, then the initial condition becomes

$$C = C_i, x > 0, t = 0$$

Where, C_i is the initial chloride content in concrete. The solution of equation (a.1.3) can then be given as:

$$C(x, t) = C_s - (C_s - C_i) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

We can obtain the diffusion coefficients by curve fitting to the above-mentioned solutions. However, the assumptions made to obtain the solutions are not always true. Firstly, it has been observed that in practice the surface chloride content C_s changes with many factors, even if the chloride concentration of the immersion solution is kept constant. Secondly, it has been seen that diffusion coefficient is a function of time and it decreases with time, especially the decrease is significant in the case of concrete containing blended cements [Thomas et al, 1999]. Thirdly, the chloride ions entering the concrete are also bound chemically or adsorbed by the concrete matrix, and both type of chlorides, i.e. free chlorides and bound chlorides exist simultaneously in chemical equilibrium. The chloride binding isotherm, i.e. the plot of free chloride vs. bound chloride, depends on many factors and is not always linear.

A1.3 Chloride Binding

It is well known that the chlorides can be bound to the hydrated cement products in concrete by physisorption and chemisorption. This binding of chlorides has influence on the diffusivity of chlorides as well as on the threshold chloride level, because only free chlorides present in pore solution are available for further diffusion and activation of passive oxide film of the reinforcement. Some of the bound chloride gets irreversibly combined into hydrate products, while some others can unbind as the free chloride concentration decreases

Since, the binding, i.e. immobilization of chloride is surely a much faster process than the diffusion process, therefore free and bound chlorides must be in equilibrium. A simplified case of chloride binding can be taken as a linear chloride binding, i.e. the ratio of fixed chloride to the free chloride is taken constant. i.e.;

$$\frac{C_b}{C_f} = K, \Rightarrow C_b = KC_f$$

where, C_b = bound chloride concentration.

C_f - free chloride concentration

K - constant, called chloride binding capacity.

Then, the fundamental one-dimensional diffusion equation changes to:

$$\begin{aligned}
 \frac{\partial C_f}{\partial t} &= D \frac{\partial^2 C_f}{\partial x^2} - \frac{\partial C_b}{\partial t} \\
 \Rightarrow \frac{\partial C_f}{\partial t} &= D \frac{\partial^2 C_f}{\partial x^2} - K \frac{\partial C_f}{\partial t} \\
 \Rightarrow \frac{\partial C_f}{\partial t} &= \frac{D}{1+K} \frac{\partial^2 C_f}{\partial x^2} \\
 \Rightarrow \frac{\partial C_f}{\partial t} &= D_{app} \frac{\partial^2 C_f}{\partial x^2}
 \end{aligned} \tag{a.1.5}$$

Equation (a.1.5) is same as (a.1.3), only difference being that D has been replaced by D_{app} , i.e. apparent diffusion coefficient, and

$$D_{app} = \frac{D}{1+K}$$

But, if the chloride binding isotherm is not linear and the relation between C_f and C_b is as: As suggested by Tang et al, 1993, where, K and n are constants.

$$C_b = KC_f^n$$

Equation (3.3.1) still holds, but the solution to this equation can only be obtained by numerical methods of integration [J. Crank]. The differential equation for diffusion in this case will be:

$$\begin{aligned}
 \frac{\partial C_f}{\partial t} &= D \frac{\partial^2 C_f}{\partial x^2} - \frac{\partial C_b}{\partial t} \\
 \Rightarrow \frac{\partial C_f}{\partial t} &= D \frac{\partial^2 C_f}{\partial x^2} - \frac{\partial C_b}{\partial C_f} \frac{\partial C_f}{\partial t} \\
 \Rightarrow \frac{\partial C_f}{\partial t} &= \frac{D}{1 + \frac{\partial C_b}{\partial C_f}} \frac{\partial^2 C_f}{\partial x^2}
 \end{aligned} \tag{a.1.6}$$

In case of much accelerated (using electric field) diffusivity tests, Tang and Nilsson, 1995, suggest that if chloride binding does not immediately reach the equilibrium, the binding rate should be considered. Xu and Chandra, 1994, suggest to use the first order chemical reaction for describing chloride binding rate, i.e.

$$\frac{\partial C_b}{\partial t} = KC_f$$

Tang and Nilsson, 1993, concluded that the chloride binding capacity of OPC concrete is strongly dependent on the content of CSH gel. They further observed that at higher concentrations (>0.01 mol/l) the chloride binding isotherm obeys Freundlich equation and at lower concentrations it obeys Langmuir equation.

11.4 Variation of diffusion coefficient with time

If the diffusion coefficient 'D' varies with time 't' only and is independent of space coordinate, then the equation (a.2.3) can be solved by introducing a new function 'T', such that

$$T = \int_0^t D(t') dt'$$

i.e., $dT = D(t)dt$

Then, equation (a.2.3) changes as

$$\begin{aligned} \frac{\partial C}{\partial t} &= D(t) \frac{\partial^2 C}{\partial x^2} \\ \Rightarrow \frac{\partial C}{\partial T} \frac{\partial T}{\partial t} &= D(t) \frac{\partial^2 C}{\partial x^2} \\ \Rightarrow \frac{\partial C}{\partial T} \partial T &= D(t) \partial t \frac{\partial^2 C}{\partial x^2} \\ \Rightarrow \frac{\partial C}{\partial T} &= D(t) \frac{\partial^2 C}{\partial x^2} \end{aligned} \quad (\text{a 1.7})$$

Equation (a.1.7) is again the same as equation (a 1.3), but for the constant 'D' replaced by unity. Therefore, we can use the solution (a.1 3.a), to get the solution in terms of 'T', which can then be converted into 't'.

To follow this approach one needs long term data for diffusion coefficients of concrete formed by using different types of blended and plain cements, so that we can find some relation between 'D' and 't'. However, much of the available data refer to relatively short-term testing (e.g., typically 1 month to 1 year).

Appendix - 2

4.2.1 Reagents and Equipments used for chloride analysis:

The chloride contents of the collected concrete powders were determined by performing potentiometric titration, with high precision, on the solutions prepared from the collected powders. The reagents used were nitric acid (HNO_3), silver nitrate (AgNO_3), sodium chloride (NaCl), hydrogen peroxide (H_2O_2), and potassium nitrate (KNO_3). All the solutions were prepared by using distilled water with the reagents.

The potentiometric titrations were performed using a high precision instrument i.e., the Metrohm's 702 SM Titrino. It is an auto titrator giving very fast and accurate results. The electrode used for potentiometric titrations in present study was ionic selective Combined Massive Ag Electrode. Besides, its sophisticated software, the equipment contains a digitally controlled electronic burette, which is capable of adding very small volume increments of the reagents at desired intervals. It also contains a magnetic stirrer with adjustable speed that keeps on stirring the solution and the added titrants while titration is in progress.

4.2.2 End point determination in titration:

The end points are localized with an algorithm, which is based in Fortuin. The greatest change in the measured potential due to single volume increment of titrant is sought. The exact end point is determined with an interpolation factor, which depends on the volume increments of titrant before and after the increment giving maximum potential change.

$$V_{EP} = V_0 + \rho * \Delta V$$

Where,

V_{EP} = Volume of titrant required to reach End Point.

V_0 = Total dispensed volume before the increment giving maximum potential change.

And, ρ = Interpolation Factor (Fortuin)

The results obtained from the instrument are very precise, if we follow the right procedure. A prerequisite of good accuracy is the correct size of the volume increment of the titrant. A good value is given when ΔV or $(V_{step}) = V_{EP}/20$. In any case, the increment size should always be between $V_{EP}/10$ and $V_{EP}/100$. Additionally, dispensing very small increments cannot increase the accuracy of the evaluation, as the change in the measured potential values would then be of the same order of the magnitude of the noise created in the process. This can produce "ghost end point".

4.2.3 Potentiometric Titration:

- (i) As mentioned earlier, Metrohm's 702 SM Titrino, an autotitrator, was used for precise and quick titrations.
- (ii) 10ml of the decanted solution was taken in a 200ml beaker and some distilled water was added to it to increase the volume, so that the massive silver electrode deeps properly in the solution.
- (iii) In case of analysis of water soluble chloride, few drops of 1:1 dilute Nitric Acid was also added to make the solution acidic.²
- (iv) All the parameters for titration were appropriately set in the autotitrator, important of which are V_{step} i.e., the volume increment of addition of 0.01N Silver Nitrate

(AgNO_3) by the electronic burette and EPC i.e., potential jump required for end point recognition V_{step} was set at 0.1ml and EPC was set as a minimum jump of 30mV or maximum of the potential jumps observed due to one volume increment of AgNO_3

(v) Before starting the actual titration the Silver Nitrate (AgNO_3) solution was first standardize against a 0.01N Sodium Chloride (NaCl) solution.

Then titrations were performed for the concrete sample solutions and percentage of chloride in the given weight of concrete powder was directly obtained from the autotitrator by feeding the required formula for calculation in the titrator.

4.2.4 Calculation of percentage of chloride in Concrete:

Let the weight of the concrete powder taken = W gm

The total volume of prepared solution from it = 50ml

We get the normality of this solution as

$$N_1 = (N_2 V_2) / V_1$$

Where, N_2 = Normality of AgNO_3 solution

V_2 = Volume of AgNO_3 dispensed to reach the end point

And, V_1 = Volume of solution taken for titration, here 10ml

Now, 50ml solution of Normality N_1

$$\begin{aligned} &= (50/1000) N_1 \text{ Equivalent Weights of } \text{Cl}^- \\ &= 0.05 N_1 * 35.5 \text{ gm of } \text{Cl}^- \\ &= 1.775 N_1 \text{ gm of } \text{Cl}^- \end{aligned}$$

Therefore,

$$\begin{aligned} \text{Percentage of chloride in concrete powder} &= [(1.775 N_1 * 100) / W] \% \\ &= [(1.775 * N_2 * V_2 * 100) / (V_1 * W)] \% \\ &= [(17.75 * N_2 * V_2) / W] \% \end{aligned}$$

This can be entered in the autotitrator as

$$RS1 = C01 * C02 * EP1 / C00$$

Where,

RS1 = Percentage of chloride

C00 = Sample size, which can be taken as weight of concrete powder
and can be entered each time we start a titration

C01 = A constant, depending upon total volume of solution made
And the volume of solution take for titration

C02 = Normality of AgNO_3 solution.

Appendix-3

c Program for Calculation of Diffusion Coefficient and Surface Concentration

```
IMPLICIT REAL*8(a-h,o-z)
Dimension XX(5), CC(5), Copt(5), C(5)
c XX Depth(cm)
c t time(sec)
c CC(i) - Observed value of Chloride Concentration at Different Depths
c C0 - Surface Concentration
c D - Optimum Value of Diffusion Coefficient
c Copt Optimum Value of Chloride Concentration at Different Depths
c for best fit

read(*,*)(CC(i),i=1,5)
read(*,*)t
pi=3.1415926
XX(1)=0.5
XX(2)=1.0
XX(3)=1.5
XX(4)=2.0
XX(5)=2.5
errmin=1000000
CC0=0.05
do 10 k=1,100
DD=5E-09
do 20 j=1,200
err=0.0
do 30 i=1,5
rX=XX(i)
X=rX/sqrt(4.0*DD*t)
call integral(X,cer)
C(i)=CC0*(1.0-cer)
30   err=err+(C(i)-CC(i))**2
err=sqrt(err)/5.0
if (err.lt.errmin) then
errmin=err
D=DD
C0=CC0
do m=1,5
Copt(m)=C(m)
enddo
endif
DD=DD+1E-09
20 continue
CC0=CC0+0.01
10 continue
write(*,*)D,C0,errmin,(Copt(i),i=1,5)
stop
end
```

```
subroutine integ_n(y,func1)
  implicit real*8(a-h,o-z)
c    y 0 1
  pi 3.1415926
  precs 0.005
  nstep v/precs
  a 0 0
  func exp(-a**2.0)
  do 100 i = 1,nstep
    a a+precs
    func func+exp(-(a**2.0))
100 continue
  func1 ((2.0*func)/sqrt(pi))*precs
  return
c    stop
  end
```